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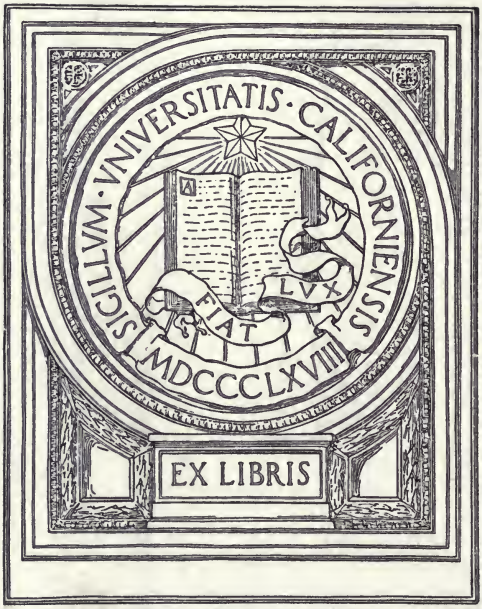
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MONOGRAPHS ON INORGANIC AND PHYSICAL CHEMISTRY

EDITED BY ALEXANDER FINDLAY, D.Sc.

THE VISCOSITY OF LIQUIDS

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BY

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Monographs on Inorganic and Physical Chemistry

EDITED BY

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To those engaged in guiding the reading of advanced students of chemistry, the difficulty of obtaining adequately summarised accounts of the progress made in recent years, more especially along certain of the more actively pursued lines of advance, becomes ever more acutely felt. So great has now become the volume of chemical investigation, and so numerous the channels of its publication, that not only the Honours Student but also the worker desirous of undertaking Research in one or other department of his subject, feels it a growing difficulty to become *au fait* with the present state of the more important and more strenuously cultivated regions of his Science. To assist these two classes of students—those reading for an Honours Degree, and those undertaking Research—is the main aim of the present Series of Monographs.

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PREFACE.

THE development of a physical property may follow two paths. Either the intrinsic importance of the property may lead to investigation from a purely physical standpoint, or its application to the elucidation of chemical constitution may cause improvements to be sought for in method, degree of accuracy, and ease of application. In the majority of physical properties utilized by the chemist, progress has gone on uniformly in each direction and a standardization of apparatus and technique has been arrived at, but in spite of a century of experimental work no very definite method has been set up for the measurement of viscosity, and no general agreement has been arrived at for the setting forth and interpretation of the results obtained. To a certain extent the inherent difficulty of understanding the strict physical meaning of viscosity is the cause of this lack of progress. The viscosity of a liquid is at least a dual phenomenon ; there is first of all the mechanical friction of molecule against molecule, and this must depend on relative molecular surface and volume ; then there is the resistance to deformation brought about by the mutual attraction of the molecules.

It follows at once that viscosity must be largely a constitutive property, and perhaps it is this fact—that so little additivity is to be looked for—that has led investigators to turn their attention to properties where a mole-

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cular value can readily be synthesized from atomic constants.

It should be borne in mind, however, that mere additivity is comparatively useless for the purpose of the chemist, who is searching for a physical confirmation of erratic chemical behaviour. When one considers, for example, such questions as the enol-keto tautomerism, the benzene problem, the effect of ring formation, and the contiguity of unsaturated groups, and the various physical methods which have been utilized for their elucidation, it will be obvious that it was the failure of the additive nature of such properties as refractive index, molecular volume, molecular magnetic rotation, and so on which turned out to be valuable. Viscosity stands out as an eminently constitutive property of the same order as optical rotatory power and the solution absorption of light. It is, therefore, of considerable importance to know how viscosity can be measured, and how the property can be utilized in the study of chemistry.

In the following pages will be given a brief description of some of the more important earlier researches which laid down the foundations of the subject, the development of a working formula, and the corrections which have been applied to it, the various apparatus which has been used at different times, and a series of chapters dealing with recent lines of work in which viscosity is playing an important part.

The authors desire to thank the Councils of the Royal Society, the Chemical Society, and the Faraday Society for permission to reproduce diagrams which have appeared in their respective Transactions; they are indebted to Prof. Washburn for Fig. 2.

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CHAPTER I.

THE DEVELOPMENT OF A WORKING FORMULA.

POISEUILLE[1] and Girard[2] carried out the pioneer work on transpiration, or the flow of liquids through capillary tubes. The former was attracted to the problem from a physiological standpoint, and not only laid down definitely the law followed by transpiring liquids, but determined with consummate accuracy the viscosity of water through a considerable range of temperature. On the basis of his experiments Poiseuille deduced the formula

$$V = \frac{KD^4H}{L}$$

where V = volume transpired in c.cm.
L = length of capillary.
D = diameter of capillary in mm.
H = pressure in mm. of mercury.
K = a factor which is constant for each liquid at a given temperature.

This empirical formula and its corrections have been substantiated mathematically by the labours of Stokes,[3] Wiedemann,[4] Hagenbach,[5] Stefan,[6] Couette,[7] Wilberforce,[8] Neumann,[9] Jacobson,[10] Knibbs,[11] Boussinesq,[12] and Brillouin.[13]

Making the assumptions that there is no slip at the surface of the capillary, that the liquid flows steadily and without eddies or turbulent motion, and that there is no kinetic energy of efflux, then the transpiration formula becomes for a liquid flowing under its own hydrostatic pressure

$$\eta = \frac{\pi}{8}\left[\frac{hgr^4}{l \times v} . d . t\right]$$

where η = the viscosity, h = the head of liquid, g = the gravitation constant, r = the radius of the capillary, d = the density of the liquid, t = the time of flow, l = the length of the capillary,

and v = the volume of the liquid which has transpired in the time t.

It is usual, however, to introduce a correction for loss of kinetic energy, viz., $-\frac{v}{8\pi l}\cdot\frac{d}{t}$ (the Couette-Finkener-Wilber-force correction).

Hence the corrected formula is $\eta = \frac{\pi}{8}\cdot\frac{hgr^4}{lv}dt - \frac{v}{8\pi l}\cdot\frac{d}{t}$.

For small pressures, high viscosities, and narrow capillaries uniformly blown out at the junctions, the correction tends to become vanishingly small, and indeed in many cases may be conveniently neglected.

This formula resolves itself into $\eta = A\,dt - B\frac{d}{t}$ where A and B are the constants for any given apparatus, and t and d are the time of flow and the density respectively. It assumes that the area of the cross section of the capillary is uniform throughout, but if this is contracted or expanded, the correction will be correspondingly affected.

Knibbs,[11] who has thoroughly investigated the recorded experiments on the viscosity of water, concludes that the correct formula should be

$$\eta = \frac{\pi}{8}\frac{hgr^4}{lv}dt - 1{\cdot}12\,\frac{v}{8\pi l}\cdot\frac{d}{t}.$$

It will be noticed that the correction term has a slightly larger value than the Couette expression.

Couette also pointed out that the modification of the stream lines at the entrance to the capillary caused loss of pressure in overcoming friction, and estimated that this could be allowed for by adding to the observed length of the capillary an amount λ equal to thrice the diameter of the above, the formula thus becoming

$$\eta = \frac{\pi hgr^4dt}{8v(l+\lambda)} - \frac{1{\cdot}12\,dv}{8\pi t\,(l+\lambda)}.$$

Bingham and White[17] deal very fully with these various corrections and the reader is referred to their paper for a detailed account of the elucidation of a working formula for the determination of absolute values of viscosity.

Viscosity and Rate of Flow.—The important work of Grün-

eisen[14] leads to a method for standardizing a viscometer which shows deviations from the Poiseuille Law. This simple law states that $\eta = p \times t \times$ const., i.e. the same liquid flowing through the same capillary at different pressures, should give a constant value for pt. Grüneisen showed that this condition is by no means rigidly fulfilled by viscometers of the Ostwald type (*vide infra*) in which the liquid flows under its own hydrostatic pressure. The variation in the values of pt is due to the fact that above a certain limiting velocity the flow is not steady but turbulent, some of the potential energy being expended in forming eddies within the liquid. Hence the liquid is not forced down the capillary so quickly as it should be if Poiseuille's Law held good, and therefore the values of pt are greater than with a slower rate of flow. It follows then that the readings of a viscometer are only trustworthy when the times of flow are sufficiently great to ensure that the product pt remains constant over the whole range of observations. Grüneisen has tested several viscometers and has published the pt curves; he has also calculated a correction to be applied where pt is no longer constant. Evidently such a correction can be rendered unnecessary by reducing the diameter of the capillary, by shortening it or by reducing the hydrostatic pressure so as to lengthen the time of flow (Applebey,[15] Merton [91]).

Bingham,[16] however, criticizes the application of Grüneisen's method and holds that the usual kinetic energy correction should be applied although it is obvious that a sufficiently long time of flow would cause $- B\frac{d}{t}$ to become vanishingly small.

The same author points out that near the entrance to the capillary the liquid is in accelerated motion for a short distance. In gaining this kinetic energy the pressure falls. The liquid at the exit end of the tube has the same velocity as at every other cross section, and its inertia carries it a considerable distance into the body of the liquid in the lower reservoir. Owing to the production of eddies this motion finally becomes disordered and disappears as heat. Bingham and White [17] measured the viscosity of water under the above conditions with a capillary which was afterwards cut into several pieces and they found that the kinetic energy corrections as demanded by the theory are directly proportional to the number of capillaries in series. The danger of

turbulent motion causing error has been dealt with by Osborne Reynolds [18] who has given an expression for this critical velocity above which eddy currents may be formed, viz. $\frac{700\,\eta}{dr}$ cms. per second.

In connexion with the experimental determination of viscosity it should be noted that the flow of liquid is influenced in a very marked way by the driving pressure that is used. Bose and Rauert have made measurements at pressures from 0·005 to 2 kilograms per sq. cm., and find that whilst Poiseuille's Law holds for low pressures, very marked deviations are found when the pressure is increased, and in some instances the relative rates of flow are reversed, the more viscous of two liquids flowing more readily and becoming the less viscous at high pressure.

Viscosity and Temperature.—Poiseuille [1] found that his experimental results for the viscosity of water could be represented by the expression $\eta_t = \eta_0/(1 + at + \beta t^2)$ where a and β are constants.

O. E. Meyer [19] suggested the formula $\eta_t = \eta_0/(1 + at)$, but this was found to apply only over a limited temperature range.

Slotte [20] proposed the equation $\eta_t = \frac{C}{a + t} - b$, where C, a and b are constants, but replaced this [21] by $\eta_t = \eta_0/(1 + \beta t)^n$ where β and n are constants.

Graetz [22] considered that the experimental data could be represented by the formula $\eta_t = \frac{A\,(\theta - t)}{t - t_1}$ in which θ = critical temperature, and t_1 = a temperature below the melting point where the viscosity is infinite.

In their classical memoir Thorpe and Rodger,[23] after a critical examination of these formulæ, found that Slotte's second expression was the best, and they used it in the representation of the viscosity at various temperatures of no less than seventy liquids.

The expression given by Slotte, when expanded on the assumption that the temperature coefficient is small, simplifies to

$$\eta = \frac{A}{1 + at + \beta t^2}.$$

In the following table are quoted some of the results obtained by Thorpe and Rodger, which will illustrate the accuracy with which the formula of Slotte agrees with the experimental numbers.

TABLE I.—Temperature Coefficients of Viscosity.

Substance.	α.	β.	$t°$.	$\eta \times 10^5$ Calc.	$\eta \times 10^5$ Observed.	Difference.
Pentane	·01044	$\cdot_0 2301$	30°	212	212	0
Iso pentane	·01088	$\cdot_0 1331$	30°	204	204	0
Hexane	·01122	$\cdot_0 3337$	60°	221	221	0
Iso hexane	·01110	$\cdot_0 3509$	60°	207	208	1
Heptane	·01214	$\cdot_0 4004$	90°	214	214	0
Iso heptane	·01199	$\cdot_0 3863$	80°	216	216	0
Octane	·01394	$\cdot_0 4926$	120°	208	208	0
Allyl iodide	·01316	$\cdot_0 3441$	100°	349	352	3
Allyl bromide	·01177	$\cdot_0 2871$	70°	315	316	1
Allyl chloride	·01111	$\cdot_0 2639$	40°	273	273	0
o-xylene	·01701	$\cdot_0 5636$	140°	249	254	5
m-xylene	·01418	$\cdot_0 3923$	130°	229	233	4
p-xylene	·01472	$\cdot_0 4578$	130°	229	233	4
Formic acid	·02870	$\cdot_0 1695$	100°	526	542	16
Acetic acid	·01826	$\cdot_0 8537$	110°	417	417	0
Propionic acid	·01720	$\cdot_0 6941$	140°	319	322	3
n-Butyric acid	·02109	$\cdot_0 1107$	160°	315	314	1
Allyl alcohol	·02552	$\cdot_0 2030$	90°	436	407	29
Water	·03580	$\cdot_0 2253$	100°	263	283	20
Acetone	·01064	$\cdot_0 3115$	50°	245	245	0

The values of α and β in the above table show that associated compounds such as water, the fatty acids and the alcohols have relatively large temperature coefficients of viscosity and that such substances, as might be expected, do not follow Slotte's expression with any great degree of accuracy. Acetic acid is an interesting case and apparently does not bear out the above statement; it must be remembered, however, that the association of this acid persists even in the state of vapour. It will be noticed, further, that in homologous series the numerical values of α and β increase with the molecular weight, but not regularly. Replacement of hydrogen by halogen raises the value of the coefficients. Fifty-five out of the seventy liquids gave differences between the observed and the calculated values of less than 5 per cent.

Brillouin[132] has reviewed the data of Thorpe and Rodger in order to elucidate the relationship between viscosity and temperature. He concludes that Slotte's formula is not the most advantageous and advocates the use of the hyperbolic formula of Graetz:—

$$\eta = A \frac{(\theta - t)}{(t - t_1)}.$$

Graetz's formula was rejected by Thorpe and Rodger as it could not be applied to water or to alcohols, but Brillouin was able to show that it represents accurately the behaviour of a large range of non-polymerized liquids and breaks down only in the case of substances which exhibit abnormally large surface tensions at lower temperatures and which may be regarded as undergoing polymerization when allowed to cool. For such compounds a more complex formula is proposed, namely

$$\eta = A \sqrt{T} . \frac{(t - t_1)^2 + C}{(t - t_o)^2 + C'},$$

where T is absolute temperature and C and C′ are constants.

Temperature of Comparison.—Although most investigators have measured the viscosity at some predetermined temperature, it is obvious that since the influence of temperature on the viscosity is different for different liquids, strictly comparable results can only be obtained when the compounds examined are at comparable temperatures. The boiling point suggests itself as the most convenient of such temperatures. It may be said at once that strictly additive relationships have not been established satisfactorily for viscosity at any one temperature although some progress has been made with its derived functions such as fluidity and the logarithm of the viscosity (p. 37).

A novel method of obtaining comparable results was devised by Thorpe and Rodger[23] who suggested that the temperatures where the viscosity-temperature curves attained equal slopes, i.e. where $\frac{d\eta}{dt}$ was the same, should be chosen and that substances for which the rate of change of viscosity was identical would probably be in a comparable physical condition. The rate of change of viscosity with temperature depends to a certain extent on the rate at which the dissociation of an associated compound is progressing, but it may be said with confidence that so far as viscosity is concerned the temperatures where the viscosity-temperature curves have equal slopes are corresponding temperatures for all substances.

By using this conception of temperatures of equal slope it has been found possible to reconstruct molecular values of viscosity which agree fairly satisfactorily with those observed. It was further shown that the ratio of the viscosities measured at two

different temperatures of equal slope is constant. For thirty-three different liquids the ratio

$$\frac{\eta \text{ at slope } 0{\cdot}0_4987}{\eta \text{ at slope } 0{\cdot}0_4323} = 2{\cdot}03 \text{ approx.}$$

was found to be practically the same, and hence it is clear that this method of comparison is independent of the value of the slope at which the comparison is made. On comparing the temperatures of equal slope in homologous series it is found, as shown by the following table, that an increment of CH_2 is accompanied by an increase in viscosity which is approximately constant.

TABLE II.—Temperatures at which the Slope is $0{\cdot}0_4323$.

Substance.	t.	Temperature Difference for CH_2.
Pentane	− 5·4°	
		25·9°
Hexane	20·5°	
		20·6°
Heptane	41·1°	
		23·0°
Octane	64·1°	
Acetone	17·8°	
		16·3°
Diethyl ketone	50·5°	
Methyl ethyl ketone	43·7°	
		12·8°
Methyl propyl ketone	56·5°	
Methyl iodide	42·9°	
		18·6°
Ethyl iodide	61·5°	
		22·1°
Propyl iodide	83·6°	
Ethyl bromide	26·9°	
		27·8°
Propyl bromide	54·7°	

CHAPTER II.

THE MEASUREMENT OF VISCOSITY.

Absolute Viscosity.—When absolute measurements of viscosity are desired it will be obvious from the formula given on page 2 that a knowledge of the driving pressure, the diameter and the length of the capillary, the volume of the liquid, the time of flow and the temperature must be obtained. The methods adopted by the earlier investigators such as Poiseuille, Graham [24], Rellstab [25], Pribram and Handl [26] are now of historical interest only. The first comprehensive attempt to determine with a high degree of accuracy the various quantities mentioned above was that of Thorpe and Rodger [23]. A diagram of the instrument used by them is given in Fig. 1. The capillary (diam. 0·008 cm.) and the bulb (5 c.c.) were designed to give a minimum time of flow of 3 minutes which could be read to 0·2 second. This time of transpiration is equivalent to a maximum velocity of 66 cm./sec. which is well within that which causes turbulent flow (Osborne Reynolds [18]). The dimensions of the capillary were determined in the usual way by weighing the mercury content and then the capillary was fused into position inside the thin glass sleeve connecting the bulbs A and B, every care being taken to avoid deformation during this process. A measured volume of liquid contained between the etched marks m_1 m_2, or m_4 m_3 was then forced through the capillary by an external pressure which could be measured by a suitable manometer. The movement of the liquid was observed by means of a telescope with cross wires, and the time of flow determined with the aid of a stop watch. The liquid was introduced into bulb A through the narrow end of the tube H_2, and any small

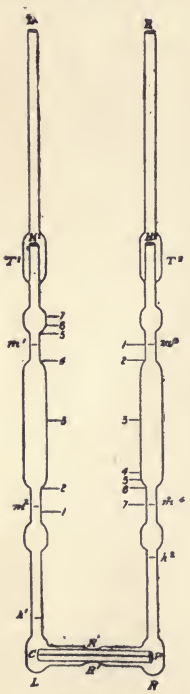


FIG. 1.

excess was expelled by applying air pressure to the tube *b* until the levels K_1 and H_2 were obtained, the surplus running over into bulb T_2. Alternate times of flow for bulbs A and B were observed and averaged. Extreme care was taken to avoid dust particles which would choke the capillary, and to this end each liquid was distilled in an all-glass apparatus until careful examination failed to detect any solid matter. Temperature control was achieved by means of a large thermostat and regulator.

Bingham and White [17] in their recent work on fluidity, criticize Thorpe and Rodger's apparatus on the grounds that it is difficult to construct and to clean, that the constants of the capillary are determined before the viscometer is built up and that the diameter of the capillary is not quite accurately known. These authors recommend a capillary of approximately 0·025 cm. diameter and 10 cm. long which is ground into side tubes quite similar to those used by Thorpe and Rodger and possessing bulbs of the capacity 2·6 c.cm. The diameter of the capillary is found by the optical method for the ends and for the middle by weighing a mercury thread. The viscometer is kept at the desired temperature in a 50 litre bath which is provided with windows, stirring gear and thermo-regulation. Bingham and White quote a series of readings for the viscosity of water which illustrates the order of the experimental error in five careful and thorough investigations, all of which were made using the capillary tube method. Hosking's [27] apparatus differed from Thorpe and Rodger's and from Bingham's merely in possessing a capillary which was attached to the bulbs by means of a rubber connexion.

The following table gives the values of the viscosity of water obtained by different investigators.

TABLE III.—Viscosity of Water.

Temperature Centigrade.	Poiseuille.	Sprung.	Slotte.	Thorpe and Rodger.	Bingham and White.
0°	0·01776	0·01778	0·01808	0·01778	0·01797
10°	0·01309	0·01301	0·01314	0·013025	0·01301
20°	0·01008	0·01003	0·01008	0·01015	0·01006
30°	0·00803	0·00802	0·00803	0·007975	0·007998
40°	0·00653	0·00657	0·00657	0·006535	0·006563
50°	—	0·00553	0·00553	0·005475	0·005500
60°	—	—	0·00472	0·00468	0·004735
70°	—	—	0·00408	0·00406	0·004075
80°	—	—	0·00358	0·00356	0·003570
90°	—	—	0·00318	0·003155	0·003143
100°	—	—	0·00285	0·00283	—

Relative Viscosity.—In the great majority of cases, however, it is not necessary to determine absolute viscosities directly and use may be made of any apparatus which has been previously calibrated with some liquid of known viscosity. The eminently simple and useful instrument designed by Ostwald ["Physico-Chemical Measurements," 1894, p. 163] has, either in its original or in a slightly modified form, been largely used by workers in this subject. The conditions necessary for rendering it an accurate and trustworthy viscometer have formed the subject of recent discussion. Reference has already been made to the investigations of Applebey, Merton, Grüneisen, and Bingham with respect to the agreement of the values obtained with this type of apparatus with Poiseuille's Law; but there still remains a source of error due to the uncertainty which arises from the variation in the water constant of the instrument. There are four reasons for the variations in the water constant: (*a*) the presence of solid particles which block up the capillary, (*b*) the solvent action of water and cleaning liquids on the capillary, (*c*) the temperature hysteresis, (*d*) the contamination of the water by the dissolved glass. To surmount these difficulties Washburn and Williams[28] have devised an improved Ostwald viscometer constructed entirely of quartz (Fig. 2).

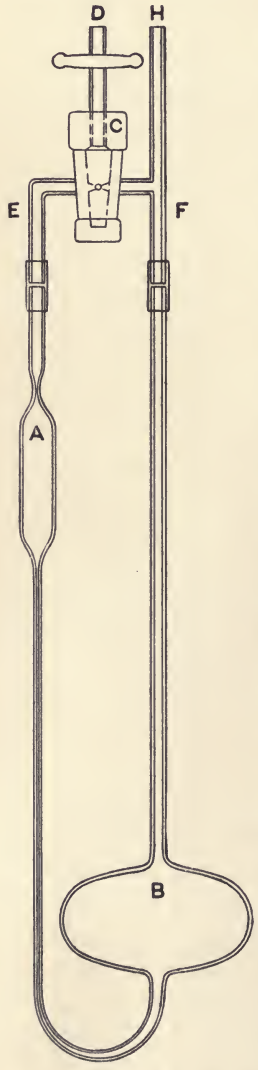


FIG. 2.

The dimensions were calculated according to Grüneisen's work so as to avoid errors due to deviations from Poiseuille's Law. The diameter of the capillary was 0·05 cm., wide enough to avoid choking by dust particles, and its length 19·5 cm. The volume of the upper bulb A was 9 c.c. and the large receiving bulb was 4·5 cm. high and 8·0 cm. wide. The mean head of liquid during its flow was 20 cm. At

the upper and lower ends of the capillary the change in diameter was made as gradual as possible so as to prevent eddy currents, whilst the constriction at the upper end of A was made symmetrical with the one at the lower end to eliminate any unequal surface tension effect when using liquids with surface tensions different from that of water. The viscometer was filled by means of a 65 c.c. pipette and the error in filling was shown to be quite negligible. The times of flow were determined by a recording chronograph operated by a motor and controlled by a standard clock, giving an error not exceeding 0·01 second. The temperature of the bath was kept constant within a few thousandths of a degree by using a large cylindrical silvered Dewar tube 50 × 12 cm. inside measurement provided with stirrer, heating coil, standard thermometer, and a Beckmann thermometer acting as a thermoscope. The liquid having been introduced, the three-way cock is attached as shown in the figure and the instrument is suspended in the bath from a metal stand and sunk until the horizontal connecting tube is immersed. The cock is then turned to connect D with the capillary arm of the viscometer and suction is applied till the bulb A is filled. The cock is then closed and turned to connect E with F. When the meniscus passes the upper mark of bulb A the observer taps the key, and repeats the operation when the meniscus passes the lower mark, the times of these two observations being recorded automatically on the chronograph tape.

Standardization of an Ostwald Viscometer.—To determine how closely a given instrument follows Poiseuille's Law, times of flow may be measured for the same liquid under different pressures or for different liquids under the same or different pressures, and since $\frac{\eta}{t \times p} = K$ where K depends only on the dimensions of the particular instrument, it follows that the $p \times t$ values should lie on a straight line.

Washburn and Williams (loc. cit.) first used the varying pressure method, connecting the viscometer with a large air reservoir and a manometer. The actual driving pressure in the viscometer is of course the sum of the manometric pressure and the head of liquid at mean time of flow, which was measured directly when half the time of flow had elapsed. The results of a series of readings are given in Table IV.

TABLE IV.—Calibration of a Viscometer.

Total Pressure in mm. of Water.	Time of Flow in Seconds.	pt.	Deviation from Mean per cent.
132·04	874·7	11550	0·04
161·51	714·6	11542	0·03
272·97	423·0	11547	0·02
294·79	391·5	11541	0·03

It is obvious that for such pressures and times of flow, Poiseuille's Law is obeyed excellently, and a value for K can be obtained since $K = \frac{\eta}{p \times t}$.

Seeing that quartz has so small a coefficient of expansion the dimensions of the instrument do not vary appreciably with temperature and accordingly the constant can equally well be determined by measuring the time of flow of water at varying temperatures under a pressure due to its own density. The formula then becomes

$$K = \frac{\eta}{t \times d}.$$

Three such measurements at 0°, 25° and 50° gave

$$\left.\begin{aligned} K_0 &= 154{\cdot}60 \times 10^{-7} \\ K_{25} &= 154{\cdot}72 \times 10^{-7} \\ K_{50} &= 154{\cdot}72 \times 10^{-7} \end{aligned}\right\} \text{ Mean } = 154{\cdot}68 \times 10^{-7}.$$

The apparatus just described have been devised for the extremely accurate determination of the viscosities of water or dilute solutions, but it by no means follows that this type of apparatus is essential or indeed desirable for all varieties of work where such a degree of accuracy is not aimed at, where the supply of material is very limited, or where special experimental difficulties are met with. To meet the special requirements of their investigations, different workers have introduced a number of modifications of the Ostwald apparatus. Thus Findlay,[29] for investigating the viscosities of mixtures of volatile liquids near their boiling points, used an Ostwald viscometer, the two limbs of which were provided with bulbs containing some of the liquid under investigation. This device effectually stopped loss by evaporation. Faust,[30] to avoid choking the capillary with dust particles, allowed it to enter the side of a wide tube, so that solid matter might sink to the bottom and not get sucked up into the capillary. Thole[39] has de-

scribed two Ostwald viscometers for use with organic liquids, where only small amounts of material are available. In these instruments horizontal capillaries, which enter the vertical limbs near the bottom, are made use of so as to avoid the entrance of solid particles. Heber Green [31] used a straight tube viscometer with two receiving bulbs, the one small for viscous liquids and the other large for more mobile fluids. The end of the tube dipped into a flask which was kept at a constant predetermined position with respect to the tube.

The Ostwald method has been used by Beck [35] up to 250° C. for fused mercury salts, and up to 600° C. by Lorenz and Kalmus [36]. Goodwin and Mailey [37] used a platinum capillary, Woelter [38] measured the rate at which a platinum wire sinks in the liquid (fused silicate), whilst Arndt [34] also proposed to measure the viscosity of fused salts by observations on the time of sinking of a weight. An ingenious method due to Scarpa [133] and slightly modified by Farrow [134] consists in measuring the time t_1 which is occupied in drawing up, through a vertical capillary tube, sufficient liquid to fill a bulb at the top of this tube, and the time t_2 which this volume takes in flowing out from the bulb under the weight of the liquid. Given constant conditions the viscosity of any liquid is proportional to the expression $\frac{t_1 t_2}{t_1 + t_2}$. The advantage of this method lies in the fact that no density determinations are necessary and that it is immaterial whether equal volumes of liquid are used in the different experiments.

Coulomb's method [32] of determining viscosity by the rate of damping of an oscillating suspended disc has not been used to any great extent owing to experimental difficulties and the need of a large volume of liquid, but Fawsitt [33] has revived its use particularly with a view to measurements on fused salts, metals, and alloys.

For a full description of the chief methods of determining viscosity, reference should be made to the work of Arndt [40].

CHAPTER III.

THE MEASUREMENT OF THE VISCOSITY OF PURE LIQUIDS PRIOR TO 1895.

ONCE a method for the measurement of viscosity had been established, attempts were made to find a connexion between this physical property and molecular weight, atomic grouping, and so on. The earliest of such investigations appears to be that of Rellstab [25] who examined some homologous series of acids, alcohols, esters, aldehydes and ketones, measuring the times of flow of equivalent weights of the substances at temperatures where their vapour pressures were equal. In brief Rellstab found that (1) the times of flow decrease as the temperature rises; (2) in an homologous series each increment of CH_2 increases the transpiration time; (3) increase of carbon diminishes whilst (4) unsaturation increases the time of flow; (5) increments of CHOH, H_2 and O increase the viscosity; (6) metamers have different viscosities. Přibram and Handl [26], using the Poiseuille method, concluded that the substitution of halogen or NO_2 for hydrogen increased the viscosity; that isomeric esters have nearly the same viscosity, but that the normal ester is more viscous than the *iso* compound; that the alcohols have a higher viscosity than the corresponding aldehydes and ketones; and that in homologous series there is a fair proportionality between the increments of viscosity and of CH_2.

Similar results were obtained by Gartenmeister [41]. Fatty alcohols and acids were shown, however, to possess remarkably high values and to give abnormal homologous relationships. Unsaturated compounds were found to be less viscous than the corresponding saturated ones.

The three series of investigations just mentioned agree in one respect, viz. their vagueness. No simple relationships are pointed out and no way is shown whereby molecular and atomic values of viscosity can be attained. In other words, the constitutive effects overshadowed the additive. These investigations, however,

cleared the way for the exhaustive researches of Thorpe and Rodger,[23] whose contribution to this subject surpasses any previous work in accuracy of measurement, wide scope of inquiry, ingenuity in manipulation and persistence in critical discussion of the experimental data. The apparatus which they used has already briefly been described.

Thorpe and Rodger determined the temperature-viscosity curves of about 70 exceptionally pure liquids, drawn from widely different families so as to include the effects of homology, substitution, isomerism and molecular complexity. They selected, as has already been mentioned (p. 6), the temperature of equal slope as that at which most truly comparable results should be obtained, and the results which they obtained lead to the following conclusions.

For unassociated liquids the viscosity increases regularly as an homologous series is ascended. An *iso* compound is generally less viscous than the normal isomeride. Allyl compounds are more viscous than *iso* propyl and less viscous than the normal propyl derivatives. Viscosity, indeed, is particularly susceptible to the arrangement of the atoms in the molecule. The substitution of chlorine, bromine and iodine for hydrogen causes a greater and greater increase in viscosity. Formic and acetic acids are highly anomalous in that they are more viscous than propionic acid. Associated liquids have a much higher viscosity temperature coefficient than unimolecular compounds have, whilst in most cases the initial members of a series show anomaly.

Recognizing that previous workers had not deduced a viscosity expression containing a molecular term, Thorpe and Rodger decided to compare not only viscosity but molecular viscosity and molecular viscosity work.

If Mv be the molecular volume of a liquid, that is the volume which contains for different substances an equal number of molecules, $(Mv)^{\frac{2}{3}}$ will represent an area over which an equal number of molecules is distributed; it may be called the *molecular surface*. The expression $\eta(Mv)^{\frac{2}{3}}$ will then represent the force in dynes required to keep a molecular surface in motion with unit velocity relative to another surface unit distance apart, and is called the *molecular viscosity*.

Since $(Mv)^{\frac{2}{3}}$ is the molecular surface $(Mv)^{\frac{1}{3}}$ will denote

molecular length, and will represent for different substances an equal number of molecules. Hence $\eta(M v)^{\frac{2}{3}} \times (M v)^{\frac{1}{3}}$ or $\eta(M v)$ represents the *molecular viscosity work*, that is the work in ergs required to move a surface equal to the molecular surface through the molecular length with unit velocity.

In their endeavour to obtain evidence of additive relationships Thorpe and Rodger compared viscosity, molecular viscosity, and molecular viscosity work not only at the boiling-point but also at temperatures of equal slope, and they found that much better results were obtained in the latter cases. To illustrate the kind of results obtained at the boiling-point the following table may be given.

TABLE V.—Viscosity at the Boiling-Point.

Substance.	$\eta \times 10^5$.	Δ CH_2.
Pentane	200	
Hexane	204	4
Heptane	199	−5
Octane	198	−1
Formic acid	536	
Acetic acid	385	−151
Propionic acid	319	−66
Butyric acid	309	−10
Methyl alcohol	329	
Ethyl alcohol	441	112
Propyl alcohol	463	22
n-Butyl alcohol	405	−58

It was found that in ascending an homologous series the viscosity coefficients diminish, but for associated compounds the differences for an increment of CH_2 vary very irregularly. For corresponding alkyl chlorides, bromides, and iodides the increasing molecular weight caused an increase in the viscosity. The *n*-propyl compounds were uniformly more viscous than the corresponding allyl compounds, whilst *iso*-derivatives were not so viscous as the normal substances. The earlier members of the series showed the anomaly which is so characteristic whatever physical property is being studied, and in general the effects of mere molecular weight were often outbalanced by association and by the arrangement of the atoms in the molecule.

Better results were obtained by considering *molecular viscosity*

at the boiling-point, and although similar conclusions to the above were found to be justified, yet sufficient additivity was discovered to make possible the calculation of atomic values and the synthesis therefrom of a molecular value.

TABLE VI.—Atomic Viscosity Constants Derived from Molecular Viscosity at the Boiling-Point.

Hydrogen	80
Carbon	− 98
Hydroxyl oxygen	196
Ethereal oxygen	35
Carbonyl oxygen	248
Sulphur	155
Chlorine	284
Iso-union	15
Double bond	113
Ring formation	610

TABLE VII.—Calculated and Observed Molecular Viscosities.

Substance.	Observed Value.	Calculated.	Difference per cent.
Pentane	480	·470	2·1
Hexane	550	532	3·3
Heptane	593	594	− ·1
Octane	646	656	1·5
Methyl alcohol	401	421	·5
Ethyl alcohol	693	483	30·3
n-Propyl alcohol	869	545	37·3
n-Butyl alcohol	883	607	31·2
Ether	459	443	3·5
Propionic acid	630	630	0
n-Butyric acid	702	692	1·4

Very similar regularities were obtained when the values of molecular viscosity work were compared, and it was found possible to synthesise satisfactory molecular values for paraffins, mono-halogen compounds, sulphides, ketones, oxides and acids, whilst unsaturated hydrocarbons, di- and poly-haloids, formic acid, benzene, water and the alcohols were quite anomalous.

Coming now to the cases when comparisons are made at temperatures of equal slope it is found that far more consistent results can be obtained. In the following table the values refer to the slope $0{\cdot}0_4323$.

TABLE VIII.—Viscosity at Temperatures of Equal Slope.

A.—*Homologous Compounds.*

Substance.	$\eta \times 10^5$.	Δ for CH_2.
Pentane	299	
Hexane	318	19
Heptane	330	12
Octane	336	6
Isoprene	295	
Diallyl	304	9
Methyl iodide	399	
Ethyl iodide	404	5
Propyl iodide	407	3
Ethyl bromide	368	
Propyl bromide	372	4
Ethylene bromide	455	
Propylene bromide	441	− 14
Methyl sulphide	335	
Ethyl sulphide	346	6 × 2
Acetone	329	
Diethyl ketone	343	7 × 2
Methyl ethyl ketone	330	
Methyl propyl ketone	344	14
Formic acid	373	
Acetic acid	370	− 3
Propionic acid	390	20
n-Butyric acid	379	− 11
Acetic anhydride	378	
Propionic anhydride	379	1
Benzene	330	
Toluene	354	24
Ethyl benzene	367	13
Iso-propyl chloride	317	
Iso-butyl chloride	331	14
Methylene chloride	372	
Ethylene chloride	377	5

B.—*Normal and Iso Compounds.*

Class.	Normal: $\eta \times 10^5$.	Iso: $\eta \times 10^5$.	Δ.
Pentanes	299	286	13
Hexanes	318	312	6
Heptanes	330	322	8
Propyl iodides	407	390	17
Propyl bromides	372	353	19
Propyl chlorides	330	317	13

C.—*Normal Propyl and Allyl Compounds.*

Class.	*n*-Propyl : $\eta \times 10^5$.	Allyl : $\eta \times 10^5$.	Δ.
Hydrocarbons	318	304	2 × 7
Iodides	407	406	1
Bromides	372	371	1
Chlorides	330	328	2

D.—*Alcohols at Slope* $0{\cdot}0_4987$.

(The curves did not admit of comparison at slope $0{\cdot}0_43323$.)

Alcohol.	$\eta \times 10^5$.	Δ for CH_2.
Methyl	650	
Ethyl	606	−44
n-Propyl	560	−46
n-Butyl	575	15
Iso-propyl	490	35
Iso-butyl	525	
Amyl	474	
Trimethyl carbinol . . .	461	29
Dimethyl ethyl carbinol . .	490	

The following conclusions may be drawn from the above viscosities at temperatures of equal slope:—

1. In homologous series there is an increase in viscosity corresponding with an increment of CH_2, but the increase tends to diminish as the molecular weight increases. The alcohols, acids, and dichlorides are abnormal.

2. In general, increase of molecular weight causes an increase in viscosity in such cases as the alkyl chlorides, bromides, and iodides.

3. *n*-Propyl compounds have a higher viscosity than the allyl derivatives.

4. *Iso* compounds are less viscous than the corresponding normal substances.

Just as molecular viscosities at the boiling-point were found to show more regularities than the simple viscosity coefficients, so at temperatures of equal slope it is better to compare derived functions of viscosity.

TABLE IX.—Molecular Viscosities at Slope $0{\cdot}0_4323$.

Substance.	$\eta\,(Mv)^{\frac{2}{3}} \times 10^4$.	$\Delta\,CH_2$.
Pentane	687	
Hexane	818	131
Heptane	931	113
Octane	1035	104
Iso-pentane	663	
Iso-hexane	799	136
Iso-heptane	908	109
Isoprene	620	
Diallyl	728	108
Methyl iodide	638	
Ethyl iodide	778	140
n-Propyl iodide	903	125
Iso-propyl iodide	878	
Iso-butyl iodide	1010	132
Ethyl bromide	663	
n-Propyl bromide	774	111
Iso-propyl bromide	750	
Iso-butyl bromide	877	127
Ethylene bromide	973	
Propylene bromide	1068	95
Iso-propyl chloride	644	
Iso-butyl chloride	760	116
Methylene chloride	600	
Ethylene chloride	737	137
Methyl sulphide	578	
Ethyl sulphide	812	2 × 117
Acetone	572	
Diethyl ketone	785	2 × 107
Methyl ethyl ketone	671	
Methyl propyl ketone	796	125
Formic acid	456	
Acetic acid	593	137
Propionic acid	742	149
n-Butyric acid	842	100
Acetic anhydride	838	
Propionic anhydride	1037	2 × 99
Benzene	688	
Toluene	821	133
Ethyl benzene	939	
o-Xylene	954	118
m-Xylene	939	
p-Xylene	923	

Careful examination of the above results shows that the increment of CH_2 in an homologous series causes a much more regular increase in viscosity than was apparent in the previous cases. With the exception of the fatty acids, some of the earlier members of the various series and the aromatic hydrocarbons, the differences are not very widely remote from the mean. It is unfortunate that Thorpe and Rodger did not investigate a few more members of each series so that this erratic behaviour of the

first one or two homologues could have been ignored. As it is the mean value for CH_2 comes to 120.

The value for the atomic viscosity of hydrogen can be obtained by subtracting the value for nCH_2 from that of $C_n H_{2n+2}$, where n is the number of carbon atoms in the molecule.

TABLE X.—Atomic Viscosity Value of Hydrogen.

Series.	n.	$\eta (Mv)^{\frac{2}{3}} \times 10^4$ for C_nH_{2n+2}.	nCH_2 Calc.	2H.
Paraffins	5	687	600	87
	6	818	720	98
	7	931	840	91
	8	1035	960	75

Knowing the values for CH_2 and for H it is obviously possible to calculate those for the halogens in CH_3I, C_2H_5 Br, etc., for the oxygen in alcohols, carbonyl oxygen in ketones and so forth.

TABLE XI.—Atomic Viscosity Value of Carbonyl Oxygen.

Substance.	$\eta (Mv)^{\frac{2}{3}} \times 10^4$.	nCH_2.	=O.	
Acetone	572	360	212	
Acetaldehyde	448	240	208	mean 198
Methyl ethyl ketone	671	480	191	
Methyl propyl ketone	796	600	196	
Diethyl ketone	785	600	185	

Similarly the other chief constants have been obtained.

TABLE XII.—Viscosity Constants at Temperatures of Equal Slope.

	Slope $0{\cdot}0_4323$.	Slope $0{\cdot}0_4987$.
Hydrogen	44·5	86
Carbon	31·0	60
Sulphur	246	474
Hydroxyl oxygen	166	320
Carbonyl oxygen	198	382
Ether oxygen	58	112
Chlorine in monochlorides	256	494
Chlorine in dichlorides	244	470
Bromine in monobromides	372	717
Iodine in monoiodides	499	962
Ring formation	244	465
Double bond	48	92
Iso union	−21	−40

It was now possible to calculate molecular values with a fair degree of accuracy from these atomic constants, and Thorpe and Rodger found that in the case of fifty compounds the average divergence of the observed from the calculated value was only about 1 per cent.

TABLE XIII.—Molecular Viscosities (× 10^4) at Slope $0{\cdot}0_4323$

Substance.	Observed.	Calculated.	Difference per cent.
Pentane	687	689	− 0·3
Hexane	818	809	1·1
Heptane	931	929	0·2
Methyl iodide	638	664	− 4·0
Ethyl iodide	778	784	− 0·8
Methyl sulphide	578	575	0·5
Diethyl ketone	785	798	− 1·6
Acetaldehyde	448	438	2·2
Acetic acid	593	604	− 1·8
Ethyl ether	635	627	1·3
Toluene	821	814	0·8
Formic acid	456	484	− 6·1
Propionic acid	742	724	2·4
n-Butyric acid	842	844	− 0·2
Methyi alcohol	358	375	4·7
Water	206	255	− 23·8

TABLE XIV.—Values for Molecular Viscosity Work at Equal Slope.

Substance.	η (Mv) × 10^3.	Δ CH_2.
Pentane	329	86
Hexane	415	80
Heptane	495	79
Octane	574	
Iso-pentane	320	85
Iso-hexane	405	77
Iso-heptane	482	
Methyl iodide	255	86
Ethyl iodide	341	84
Propyl iodide	425	
Ethyl bromide	282	71
Propyl bromide	353	
Methyl sulphide	240	2 × 77
Ethyl sulphide	393	
Acetone	238	2 × 69
Diethyl ketone	376	
Methyl ethyl ketone	302	81
Methyl propyl ketone	383	
Formic acid	160	77
Acetic acid	237	87
Propionic acid	325	73
n-Butyric acid	397	
Benzene	314	82
Toluene	396	79
Ethyl benzene	475	

It is again noteworthy that the earlier members of a series and also associated compounds show considerable abnormality.

When the data are calculated in terms of molecular viscosity work, η (Mv), the relationships which are obtained closely resemble those for molecular viscosity.

The average value for CH_2 was found to be 80. In the same way as before, atomic constants were calculated, and the following values obtained.

TABLE XV.—Atomic Viscosity Work Constants.

	At Slope 0·04323.	At Slope 0·04987.
Hydrogen	− 34	− 64
Carbon	148	278
Hydroxyl oxygen	100	188
Ethereal oxygen	43	73
Carbonyl oxygen	− 19	− 36
Sulphur	144	271
Chlorine in monochlorides	89	167
Chlorine in dichlorides	82	154
Bromine in monobromides	151	284
Iodine in monoiodides	218	410
Ring formation	−369	−694
Double bond	− 95	−179
Iso-union	− 8	− 15

The above summary of Thorpe and Rodger's work shows that additive relationships become apparent only when proper temperatures are selected for making the comparison. Even then, compounds which are notably associated or in the case of which constitutional influences are at work, fall outside the scope of the additive law. The effects of the homologous increment, for example, gradually diminish as a series is ascended and when atoms or groups possessing much residual affinity are present in a molecule, considerable departure from the calculated values is observed. This is clearly shown in the case of the chlorine substitution derivatives of methane (Table XVI.).

TABLE XVI.—Effect of Substitution.

Substance.	Mol. Viscosity × 10^4 at Slope 0·04323.	Δ for Cl.
Methyl chloride	420 (calc.)	
		180
Methylene chloride	600	
		147
Chloroform	747	
		107
Carbon tetrachloride	854	

Each additional chlorine atom produces less and less effect on the molecular viscosity.

Reference has already been made to the anomalous behaviour of the alcohols; this is more clearly seen from the following table.

TABLE XVII.—The Alcohols.

Substance.	$\eta \times 10^5$.	Δ.	$\eta (Mv)^{\frac{2}{3}} \times 10^4$.	Δ.	$\eta (Mv) \times 10^3$.	Δ.
Water	—	—	390	362	105	155
Methyl alcohol	650	− 44	760	173	260	107
Ethyl alcohol	606	− 46	933	108	367	82
n-Propyl alcohol	560	15	1041	191	449	121
n-Butyl alcohol	575		1232		570	
Iso-propyl alcohol	490	35	930	107	405	124
Iso-butyl alcohol	525		1137		529	
Trimethyl carbinol	461	29	1020	170	480	47
Dimethyl ethyl carbinol	490		1190		527	

It is obvious that there is no constant difference for the homologous increment in these cases and it is quite impossible to calculate a molecular value from the atomic constants previously given. This is by no means surprising, for the peculiar influence of association on viscosity has been pointed out by almost every worker in the subject. At the same time it must be emphasized again that Thorpe and Rodger had not sufficient material at their disposal to deal adequately with the question of atomic constants, and it is only recently that an attempt has been made to investigate a large number of homologous series each containing as many members as can conveniently be prepared.

CHAPTER IV.

THE MEASUREMENT OF THE VISCOSITY OF PURE LIQUIDS SUBSEQUENT TO 1895.

Temperature Co-efficients of Viscosity.—Although the work of Thorpe and Rodger did not go far enough to afford a final method of representing viscosity data, little has been done up to the present time to put the matter on a satisfactory basis. Brief reference may be made to the work of Mühlenbein [42] and of Wagner and Mühlenbein [43] which confirmed previous work on the effects of substitution in the benzene series; to that of Beck [44] who found that in homologous series there is a proportionality between viscosity and molecular weight, that *iso*-compounds are less viscous than normal isomers, and that the abnormally high viscosities of the alcohols and acids depends on the presence of potentially quadrivalent oxygen.

The next real advance is due to Bingham [45] who pointed out that relationships of a more general and regular character are obtained when one considers not the viscosity but the reciprocal of the viscosity, or the *fluidity*. To the work of Bingham somewhat fuller consideration must be given.

Formulæ for Fluidity.—The fact that the mixture law is so rarely observed led Bingham to make use of the reciprocal of viscosity, or fluidity. Using the data of Thorpe and Rodger, Linebarger, and Dunstan, he found that mixtures which gave a sagged viscosity curve yielded a linear fluidity curve and naturally deduced that fluidity was an additive property. On applying this deduction to pure liquids it was found that the fluidity of unassociated compounds was very markedly proportional to the absolute temperature, and even for associated liquids this proportionality was found to hold good at sufficiently high temperatures.

The simple linear formula, however, was replaced by the expression

$$\phi = \frac{c}{\phi - at - b} \quad . \quad . \quad . \quad (1a)$$

containing three constants a, b and c, and again by

$$t = A\phi - \frac{B}{\phi} + C \quad . \quad . \quad . \quad (1b)$$

These formulæ are really equivalent when

$$A = \frac{1}{a}, \; B = \frac{c}{a} \text{ and } C = -\frac{b}{a}.$$

The above fluidity formulæ proved capable of representing a considerable amount of viscosity data with an ease and accuracy unequalled by any formula hitherto proposed, but an expression containing four constants was found necessary to reproduce the experimental values for water and hydroxylated compounds in general, viz. :—

$$t = A\phi + \frac{B}{\phi + D} + C \quad . \quad . \quad . \quad (2)$$

Since a relationship may be reasonably expected to exist between fluidity and volume, van der Waals's equation

$$T = \frac{pv}{R} - \frac{pb}{R} + \frac{a}{Rv} - \frac{ab}{Rv^2}$$

might be recast in terms of fluidity as

$$T = a\phi - \beta + \frac{\gamma}{\phi} - \frac{\delta}{\phi^2} \quad . \quad . \quad . \quad (3)$$

where a, β, γ, δ are constants, and T represents the absolute temperature corresponding to a given fluidity ϕ. The applicability of this formula is shown by the following table.

TABLE XVIII.—Fluidity Calculated and Observed.

A.—*Water.**

Absolute Temperature.		Percentage Difference.
Observed.	Calculated.	
273·37°	273·37°	—
274·13°	273·99°	−0·05
276·09°	275·53°	−0·20
278·45°	277·62°	−0·29
286·53°	285·80°	−0·25
303·72°	303·72°	−0·00
320·03°	320·28°	+0·07
373·00°	373·00°	—

* The experimental data are from the work of Thorpe and Rodger.

B.—*Octane.**

Absolute Temperature.		Percentage Difference.
Observed.	Calculated.	
273·25°	273·25°	—
295·92°	295·33°	−0·19
316·89°	316·88°	0·00
339·46°	339·75°	0·08
361·33°	361·52°	0·05
395·07°	395·05°	—

The above table shows that a formula based on van der Waals's equation reproduces fluidity data somewhat better than one which contains three constants only. It is, however, not so accurate as formula (2) which also contains four constants.

TABLE XIX.—Average Percentage Differences from using the Equations (1*b*), (2), and (3).

Substance.	Average per cent Difference from (1b).	Average per cent Difference from (2)	Average per cent Difference from (3)
Water	0·17	0·01	0·09
Octane	0·16	0·02	0·08
Iso-butyric acid . . .	0·43	0·06	0·11
Active amyl alcohol . .	1·17	0·08	0·38

Additive Relations.—The additive nature of the relationships is seen more clearly when attempts are made to deduce atomic constants at some fixed value of the fluidity, where, according to Bingham, a truly "corresponding condition" is to be looked for.

In the following tables are given the values of the absolute temperature corresponding with a fluidity value of 300 in C.G.S. units ("Amer. Chem. Journ.," 1910, **43**, 302). The absolute temperature values corresponding with the fluidity 200 have been calculated by Bingham and Miss Harrison ("Zeitschr. physikal. Chem.," 1909, **66**, 1).

* The experimental data are from the work of Thorpe and Rodger.

TABLE XX.—Temperature Value of a Methylene Grouping at Fluidity 300.*

Substance.	Absolute Temperature Observed.	Temperature Value, CH_2.
Pentane	258·2°	30·5°
Hexane	288·7°	
Heptane	313·1°	24·4°
Octane	337·8°	24·7°
Iso-pentane	253·8°	29·2°
Iso-hexane	283·0°	
Iso-heptane	305·3°	22·3°
Isoprene	250·0°	24·4°
Diallyl	274·4°	
Methyl iodide	338·5°	20·8°
Ethyl iodide	359·3°	
Propyl iodide	382·5°	23·2°
Iso-propyl iodide	371·6°	23·5°
Iso-butyl iodide	595·1°	
Ethyl bromide	311·5°	29·0°
Propyl bromide	340·5°	
Iso-propyl bromide	331·0°	26·8°
Iso-butyl bromide	357·8°	
Iso-propyl chloride	289·8°	32·7°
Iso-butyl chloride	322·5°	
Methyl propyl ether	265·5°	22·9°
Ethyl propyl ether	288·4°	
Dipropyl ether	314·2°	25·8°
Methyl *iso*-butyl ether	284·9°	19·6°
Ethyl *iso*-butyl ether	304·5°	

The mean value of a methylene grouping is 25·4°.

TABLE XXI.—Temperature Value of the Iso Grouping at Fluidity 300.

Substance.	Normal.	Iso.	Temperature Value.
Pentane	258·2°	253·8°	4·4°
Hexane	288·7°	283·0°	5·7°
Heptane	313·1°	305·3°	7·8°
Propyl iodide	382·5°	371·6°	10·9°
Propyl bromide	340·5°	331·0°	9·5°
Propyl chloride	298·7°	289·8°	8·9°
Butyric acid	426·5°	416·7°	9·8°
Methyl butyrate	343·2°	334·2°	9·0°

The temperature of equal fluidity is, on the average, 8·2° lower in the case of the *iso*- than in the case of the normal compound.

* The experimental data are from the work of Thorpe and Rodger.

TABLE XXII.—Temperature Value for Hydrogen at Fluidity 300.

Substance.	*n*.	Temperature Observed.	Calc. for $n \times CH_2$.	Temperature Value of 2H.
Pentane	5	258·2°	127·0°	131·2°
Hexane	6	288·7°	152·4°	136·3°
Heptane	7	313·1°	177·8°	135·3°
Octane	8	337·8°	203·2°	134·6°

Hence the mean value for H is 67·8, and for carbon, – 110·2.

TABLE XXIII.—Temperature Value for Double Bond at Fluidity 300.

Derivative Substance.	Normal Propyl.	Allyl.	Temperature Value of Double Bond.
Iodide	382·5°	380·5°	2·0°
Bromide	340·5°	336·5°	4·0°
Chloride	298·7°	291·9°	6·8°

Hence the temperatures of equal fluidity are, in the case of an allyl compound, about 4·3° lower than for the normal propyl compound, which contains two atoms of hydrogen more. Hence a double bond has a temperature value of 131·3°.

TABLE XXIV.—Temperature Value of Oxygen at Fluidity 300.

Substance.	Absolute Temperature.		Temperature Value of – O –.
	Observed.	Calculated for C_nH_{2n+2}.	
Methyl propyl ether . .	265·5°	237·2°	28·3°
Ethyl propyl ether . .	288·4°	262·6°	25·8°
Dipropyl ether . .	314·2°	288·0°	26·2°
Methyl *iso*-butyl ether . .	284·9°	254·4°	30·5°
Ethyl *iso*-butyl ether . .	304·5°	279·8°	24·7°

The average value for – O – *is* 27·1°.

TABLE XXV.—Value of the Benzene Ring at Fluidity 300.

Substance.	Absolute Temperature.		Temperature Value of the Benzene Ring.
	Observed.	Calculated for C_nH_{2n-6}.	
Benzene	348·1°	139·5°	208·6°
Toluene	347·5°	164·9°	182·6°
Ethyl benzene	362·1°	190·3°	171·8°
o-Xylene	377·5°	190·3°	176·2°
m-Xylene	355·5°	190·3°	164·2°
p-Xylene	357·4°	190·3°	167·1°

The minimum value 164·2 was chosen to avoid error due to "unlike association".

In Table XXVI are grouped together for comparison the constants at fluidities 200 and 300.

TABLE XXVI.—Constants at Fluidity 200 and Fluidity 300.

Atom or Grouping.	$\phi = 200$.	$\phi = 300$.
Carbon	− 95·7	− 110·2
Hydrogen	59·2	67·8
Oxygen	24·2	27·1
Iso-union	− 7·6	− 8·2
Double bond	114·4	131·3
Benzene ring	141·8	164·2

A few illustrations may be given showing the application of these values in constructing a "molecular temperature" at fluidity 300.

Hexane. C_6H_{14}.

Observed Value 288·7.

C_6 =	− 661·2
H_{14} =	949·2
C_6H_{14} =	288·0.

Dipropyl ether. $(C_3H_7)_2O$.

Observed Value 314·2.

C_6 =	− 661·2
H_{14} =	949·2
O =	27·1
$C_6H_{14}O$ =	315·1

Methyl Butyrate. $C_3H_7CO.O.CH_3$. $= C_5H_{10}O_2$

Observed Value 343·2.

C_5 =	− 551·0
H_{10} =	678·0
O_2 =	54·2
Double bond =	131·3
$C_5H_{10}O_2$ =	312·5

Where, however, a compound is associated, Bingham considers that the ratio between the observed and calculated results (as in the case of methyl butyrate) should give the association factor since the value of the constants are additive. Such a list of association factors is given in Table XXVII.

TABLE XXVII.—Association Factors at Fluidity 300.

Substance.	Absolute Temperature.		Association Factor.
	Observed.	Calculated.	
Water	358·5°	162·7°	2·20
Dimethyl ketone	289·5°	207·5°	1·23
Diethyl ketone	326·5°	285·4°	1·14
Methyl ethyl ketone	315·6°	260·0°	1·21
Methyl propyl ketone	330·0°	285·4°	1·17
Acetic acid	407·9°	236·3°	1·73
Propionic acid	408·5°	261·7°	1·55
n-Butyric acid	426·5°	287·1°	1·48
Acetic anhydride	388·1°	309·9°	1·25
Propionic anhydride	402·4°	360·7°	1·11
Benzene	348·1°	303·7°	1·14
Toluene	347·5°	329·1°	1·06
Ethyl benzene	362·1°	354·5°	1·02
Methyl alcohol	336·9°	188·1°	1·79
Ethyl alcohol	371·5°	213·5°	1·74
Methyl formate	297·5°	236·3°	1·26
Ethyl formate	311·4°	261·7°	1·19
n-Propyl formate	333·9°	287·1°	1·16
Methyl acetate	306·0°	261·7°	1·17
Ethyl acetate	320·8°	287·1°	1·12
n-Propyl acetate	343·0°	312·5°	1·11

Interesting as is the above method of calculating the degree of association of a liquid, still too great stress ought not, in the present condition of our knowledge, to be laid on the actual values so obtained, for it must be borne in mind that the differences between the first and second columns are due not only to association but to want of sufficient data for calculating accurately the atomic "constants" and also to constitutional effects, such as mutual influence of groupings in the molecule, symmetry and so forth.

The Relation between Fluidity and Vapour Pressure.—The fact that the fluidities of saturated aliphatic hydrocarbons and of ethers are for each class practically identical at the boiling-points of the substances suggests the question whether this relation holds for other temperatures of equal vapour pressure. Using the

vapour pressure determinations of Young and his collaborators and also independent observations of his own, Bingham (loc. cit.) finds that the fluidity-vapour pressure curves for ethers and hydrocarbons are entirely similar and indicate that at a sufficiently high temperature, fluidity is a linear function of the vapour pressure. It follows then for ethers and hydrocarbons that at temperatures corresponding to any given fluidity the vapour pressures of these compounds are equal, and hence when liquids of a given class have equal fluidities they are in a corresponding condition.

Viscosity Relations.—Although it is fairly evident that no method of obtaining additive relationships can expect to be trustworthy till a larger mass of data is available, yet attention was drawn by Dunstan and Thole [46] to the fact that a fairly exact

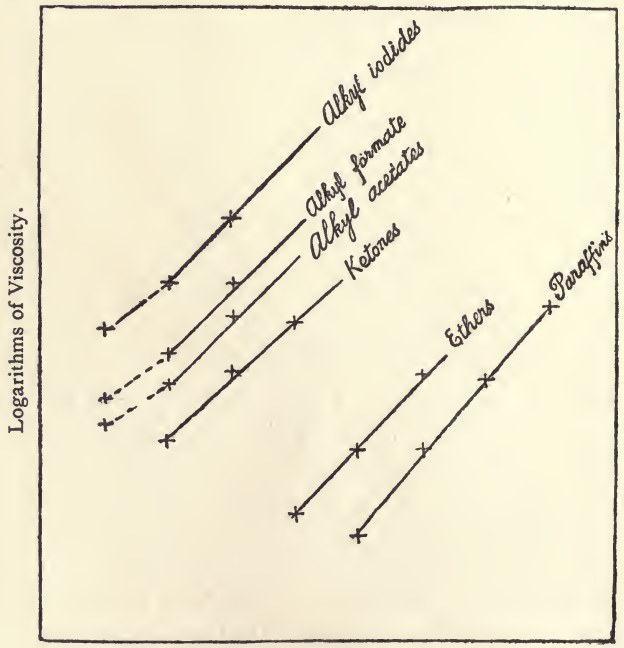


FIG. 3.—Molecular weights.

linear relationship exists between molecular weights and logarithms of viscosity in several homologous series. In one of these series, the methyl alkyl carbinols, all the eight members, ranging from *iso*-propyl alcohol to methyl-nonyl-carbinol were found to give log. viscosities which lie on a straight line. In the other series,

the *iso*-propyl alkyl carbinols, the agreement is scarcely so good, but a glance at the figure will show that a straight line adequately represents the relationship between molecular weight and the logarithm of the viscosity, in the case, at least, of the higher members of a series. A long series of dibasic esters from the

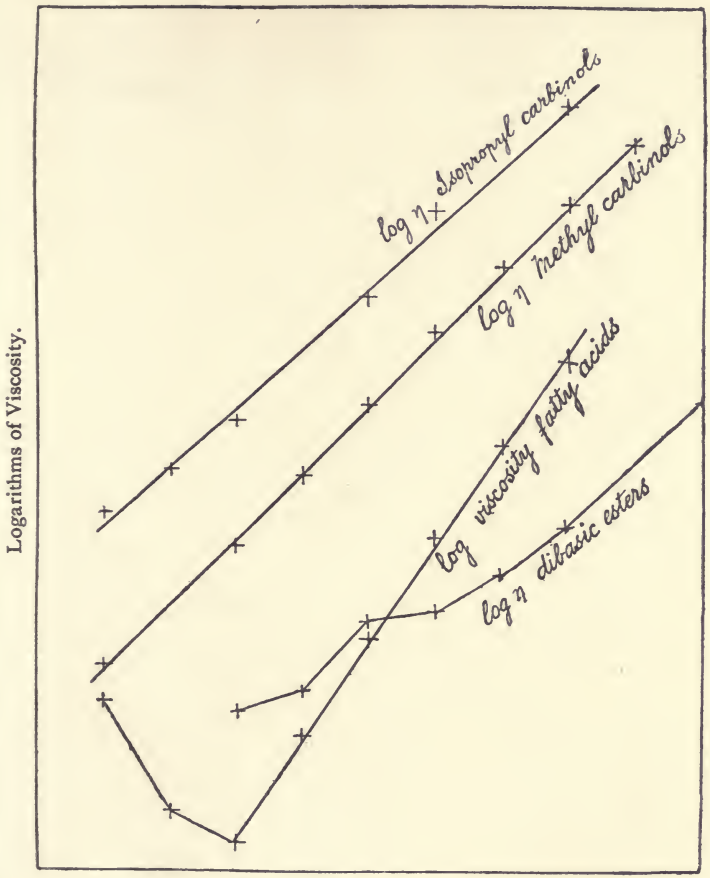


FIG. 4.—Molecular weight.

oxalic to the sebacic term shows little regularity until the first three members are passed, since conjugation effects are pronounced in these cases, but from glutaric ester onwards the linearity of the curve becomes marked. Gartenmeister [47] measured the viscosities of the first nine members of the fatty acids at 20°, and on plotting log. viscosity against molecular

weight a linear curve is afforded from the third member onwards. Adding to these cases, all of which embody a homologous series of some length, the measurements of Thorpe and Rodger [23] for the first four or five members of some ten homologous series, the same linear relationship is found to obtain and hence additive values of log. viscosity for the more important elements and radicles can be calculated.

It should be mentioned that hydroxylated compounds, which almost invariably give abnormally high values for viscosity, are not suitable for the purpose of such a calculation, as is apparent when the slope of the curves is considered. Whereas in Fig. 8 the log.-viscosity-molecular-weight curves for such groups as the paraffins, ethers, esters, and ketones are parallel, it will be seen in Fig. 4 that the curve for the acids is by no means parallel to that for the carbinols. Further, as with almost every physical property, the results for the first one or two members of a homologous series tend to be anomalous, and should not be included.

In the following tables the data of Thorpe and Rodger at 20° have been taken as a basis for the calculated values, while the logarithms of viscosity have been multiplied by 10^5 to avoid barred characteristics.

TABLE XXVIII.—Methyl Alkyl Carbinols at 25°.

	Viscosity.	Log $\eta \times 10^5$.	ΔCH_2.
Iso-propyl alcohol	0·0206	3·3139	
Methyl *n*-propyl carbinol . . .	0·0309	3·4901	0·0881
Methyl *n*-butyl carbinol . . .	0·0398	3·6001	0·1100
Methyl *n*-amyl carbinol . . .	0·0506	3·7037	0·1036
Methyl *n*-hexyl carbinol . . .	0·0655	3·8162	0·1125
Methyl *n*-heptyl carbinol . . .	0·0828	3·9180	0·1018
Methyl *n*-octyl carbinol . . .	0·1010	4·0043	0·0863
Methyl *n*-nonyl carbinol . . .	0·1228	4·0892	0·0849

TABLE XXIX.—Iso-Propyl Alkyl Carbinols at 25°.

	Viscosity.	Log $\eta \times 10^5$.
Methyl *iso*-propyl carbinol . . .	0·0351	3·5449
Ethyl *iso*-propyl carbinol . . .	0·0403	3·6050
n-Propyl *iso*-propyl carbinol . . .	0·0474	3·6761
n-Butyl *iso*-propyl carbinol . . .	0·0709	3·8505
n-Amyl *iso*-propyl carbinol . . .	0·0729	3·8629
n-Hexyl *iso*-propyl carbinol . . .	0·1018	4·0077
n-Octyl *iso*-propyl carbinol . . .	0·1431	4·1557

A marked abnormality in the fourth member disturbs the regularity of this series and interferes with it as a means of obtaining CH_2 values.

TABLE XXX.—Esters of the Oxalic Series at 25°.

	Viscosity.	Log $\eta \times 10^5$.	ΔCH_2.
Diethyl oxalate	0·01751	3·2433	
,, malonate	0·01875	3·2730	
,, succinate	0·02400	3·3802	
,, glutarate	0·02480	3·3945	
,, adipate	0·02768	3·4425	
,, pimelate	0·03280	3·5160	0·0899
,, suberate	0·04036	3·6059	0·0994
,, sebacate	0·05073	3·7053	

This series shows anomaly up to the glutaric member.

TABLE XXXI.—Fatty Acids at 20°.

	Viscosity.	Log $\eta \times 10^5$.	ΔCH_2.
Formic acid	0·01804	3·2562	
Acetic ,, ...	0·01232	3·0906	
Propionic ,, ...	0·01107	3·0441	
Butyric ,, ...	0·01598	3·2036	0·1595
Valeric ,, ...	0·02236	3·3495	0·1459
Hexoic ,, ...	0·03201	3·5053	0·1558
Heptoic ,, ...	0·04356	3·6391	0·1338
Octoic ,, ...	0·05749	3·7596	0·1205
Nonoic ,, ...	0·08319	3·9201	0·1605

TABLE XXXII.—The Value for CH_2.

Substance.	η.	$\Delta \log \eta \times 10^5$ for CH_2.	
Hexane	0·00320		
Heptane	0·00411	0·109	0·109 paraffins
Octane	0·00538	0·117	
Iso-hexane	0·00300	0·102	
Iso-heptane	0·00379		
Ethyl iodide	0·00583	0·102	0·102 alkyl iodides
Propyl ,,	0·00737	0·101	
Iso-propyl iodide	0·00690		
Iso-butyl ,,	0·00870		
Methyl propyl ether	0·002515	0·101	
Ethyl ,, ,,	0·003175		
Propyl ,,	0·00420	0·126	0·108 ethers
Ethyl ,,	0·002345		
Propyl ,,	0·00420	0·111	
Methyl propyl ,,	0·002515		
,, *iso*-butyl ,,	0·003065	0·092	
Ethyl ,, ,,	0·003785		
Ethyl acetate	0·00449		
Propyl ,,	0·00581	0·112	0·107 esters
Methyl propionate	0·00454	0·103	
,, butyrate	0·00575		
Acetone	0·003225		
Methyl propyl ketone	0·00501	0·096	0·106 ketones
,, ethyl ,,	0·00423	0·117	
Acetone	0·00501		
Propyl alcohol	0·0226		
Butyl ,,	0·0295	0·116	0·116 alcohols
Iso-butyl ,,	0·0391	0·115	
Iso-amyl ,,	0·0509		
Methyl sulphide	0·00293	0·091	0·091 sulphides
Ethyl ,,	0·00455		

Mean value for 16 pairs = 0·107.

Value at 20° of log $\eta \times 10^5$ for the Chief Groups.

Hydrogen.—Subtracting the CH_2 value from log $\eta \times 10^5$ of the paraffins:—

From hexane	0·931	Mean for H = 0·934.
,, heptane	0·932	
,, octane	0·938	

Alcoholic Hydroxyl.—Subtracting the value for CH_2 and H from the log $\eta \times 10^5$ of the higher alcohols:—

From propyl alcohol	2·097	Mean for OH = 2·102.
,, butyl ,,	2·108	

Ethereal Oxygen.—Subtracting the value for the alkyl radicles from the log $\eta \times 10^5$ of the ethers:—

From methyl propyl ether	0·105	Mean for O = 0·098.
,, ethyl ,, ,,	0·099	
,, propyl ether	0·113	
,, ethyl ,,	0·074	

Carbethoxyl.—Subtracting the value for the alkyl radicles from log $\eta \times 10^5$ of the higher fatty esters :—

From ethyl propionate	1·583	Mean for CO_2Et = 1·573.
,, ,, butyrate	1·570	
,, ,, valerate	1·566	

Carbon.—Subtracting the value for hydrogen from that of CH_2 :—

$$C = -1{\cdot}761.$$

Carbonyl (ketonic).—Subtracting the value of the alkyl radicles from log $\eta \times 10^5$ of the ketone :—

From acetone	0·427	Mean for CO = 0·407.
,, methyl ethyl ketone	0·437	
,, ,, propyl ,,	0·404	
,, diethyl ketone	0·372	

Iso-Union.—Subtracting the value for the normal compounds from those of the *iso*-isomeride :—

From *iso*-hexane – hexane	– 0·028	Mean for *iso*-union = – 0·030.
,, *iso*-heptane – heptane	– 0·035	
,, *iso*-propyl bromide – propyl bromide	– 0·030	
,, *iso*-propyl iodide – propyl iodide.	– 0·029	

Double Bond.—Subtracting the value for the saturated compound from those of the unsaturated body and two H values :—

From allyl iodide + 2H – propyl iodide	1·862	Mean for double bond 1·847.
,, ,, bromide + 2H – propyl bromide	1·850	
,, ,, chloride + 2H – propyl chloride	1·840	
,, ½ [diallyl + 4H – hexane]	1·835	

Collected Values at 20°.

CH_2	0·107	O (ethereal)	0·098
H	0·934	CO_2Et	1·573
OH (alcoholic)	2·102	C	– 1·761
CO (ketonic)	0·407	*Iso*-union	– 0·030
Double bond	1·847		

Owing to the additive character of the logarithms of viscosity, it becomes possible to calculate, with fair accuracy, the viscosity of a compound from the values of the atomic and group constants just given, as the following examples indicate :—

(1) *Ethyl Diethylacetoacetate.* η_{20}° = 0·0344 (Gartenmeister).

$CH_3{\cdot}CO{\cdot}CEt_2{\cdot}CO_2Et$:

6 CH_2	=	0·642
H	=	0·934
CO	=	0·407
CO_2Et	=	1·573
		3·556 = log of 0·0360 × 10^6.

(2) *Iso-Butyl Ethyl Ether.* $\eta_{20}° = 0{\cdot}0376$ (Thorpe and Rodger).

$(CH_3)_2CH{\cdot}CH_2{\cdot}O{\cdot}C_2H_5$:

$6CH_2$	$= 0{\cdot}642$
O	$= 0{\cdot}098$
2H	$= 1{\cdot}868$
	$2{\cdot}608$
iso	$= -\ 0{\cdot}030$
	$2{\cdot}578 = \log$ of $\mathbf{0{\cdot}0378} \times 10^5$

(3) *Iso-Amylene.* $\eta_{20}° = 0{\cdot}00212$ (Thorpe and Rodger)

$(CH_3)_2CH{\cdot}CH : CH_2$:

$5CH_2$	$= 0{\cdot}535$
	$= 1{\cdot}847$
	$2{\cdot}382$
iso	$= -\ 0{\cdot}030$
	$2{\cdot}352 = \log$ of $\mathbf{0{\cdot}0225} \times 10^5$

(4) *Ethyl Acetoacetate.* $\eta_{20}° = 0{\cdot}0168$ (Gartenmeister).

Ketonic.

$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2Et$

$2CH_2$	$= 0{\cdot}214$
H	$= 0{\cdot}934$
CO	$= 0{\cdot}407$
CO_2Et	$= 1{\cdot}573$
	$3{\cdot}128 = \log$ of $\mathbf{0{\cdot}0134} \times 10^5$

Enolic.

$CH_2{\cdot}C(OH){:}CH{\cdot}CO_2Et$

$2CH_2$	$= 0{\cdot}214$
OH	$= 2{\cdot}102$
CO_2Et	$= 1{\cdot}573$
	$= 1{\cdot}847$
	$5{\cdot}736$
C	$= -\ 1{\cdot}761$
	$3{\cdot}975 = \log$ of $\mathbf{0{\cdot}0944}$

Therefore, percentage of enolic form $= 4{\cdot}2$.

CHAPTER V.

THE VISCOSITY OF LIQUID MIXTURES.

THE viscosity of binary liquid mixtures has been a subject of frequent investigation but up to the present no formula has been deduced which will satisfactorily reproduce the experimental facts. No linear formula can be utilized since in every curve there is a divergence, greater or less, from that demanded by the mixture law. In the majority of cases a sagging takes place in the viscosity concentration curve, and since it is hardly conceivable that two substances should be entirely indifferent towards each other, this, in general, slight departure from linearity may be accounted for by an equally slight mutual action. Further, it should be noted that the divergences become less with elevation of the temperature, a fact which again leads to the assumption that the exercise of some residual affinity leading to the formation of loosely aggregated complexes may be postulated.

Historical.—Brief reference may be first made to the earlier work in this direction.

Poiseuille,[1] who appears to have been the first investigator to attack the problem of the viscosity of liquid mixtures, found that the ethyl alcohol-water pair gave a maximum viscosity at about the composition represented by $C_2H_6O.3H_2O$. Graham [24] discovered that aqueous solutions of many common acids and alcohols give similar maxima at points corresponding with simple molecular concentration, e.g. $H_2SO_4.H_2O$; $CH_3COOH.H_2O$; $HCl.12H_2O$.

Wijkander [48] followed this up with an investigation of the viscosities of binary mixtures of acetic acid, water, aniline, benzene, ether chloroform, carbon disulphide and ethyl alcohol. Such of the above pairs as mixed without appreciable change gave more or less sagged curves, ether-chloroform and ether-carbon disulphide afforded inflected curves, but the aqueous solu-

tions of acetic acid showed, at various temperatures, a distinct drift in the position of the maximum point. This behaviour was observed also by Noack [49] in connexion with aqueous ethyl alcoholic solutions, by Traube [50] and by Pagliani and Battelli [51] for aqueous alcohols and acids. Linebarger [52] investigated binary mixtures of ethyl acetate, carbon bisulphide, carbon tetrachloride, chloroform, nitrobenzene, ethyl iodide, toluene, ethyl benzoate and ether. In nearly all these cases the observed viscosity was less than that calculated from the mixture law but for the liquid pairs benzene-toluene and toluene-carbon disulphide, a very slight sag indeed was perceptible. Thorpe and Rodger [53] extended their work on the viscosity of pure liquids to that of liquid mixtures, viz. benzene—carbon tetrachloride ; methyl iodide-carbon disulphide and ether-chloroform. In none of these cases was the mixture law observed, the third pair giving an inflected curve, which suggests possible combination between the components. Varenne and Godefroy [54] found a series of discontinuities on the viscosity-concentration curve of ethyl alcohol-water and considered these as evidence for the existence of several hydrates in solution. Wagner and Mühlenbein [55] quoted several cases of the occurrence of maximum and minimum points. Benzonitrile, nitromethane, and allyl *iso*-thiocarbimide depress the viscosity of ethyl alcohol, whilst nitrobenzene lowers that of *iso*-butyl alcohol ; *o*-nitrotoluene in ethyl alcohol gives an inflected curve and *p*-nitrotoluene in the same solvent shows a minimum point. Dunstan [56] investigated a considerable number of binary mixtures and concluded that viscosity concentration curves of binary mixtures could be classified as follows :—

Type I.—Those which obey approximately the mixture law, being concave to the axis of percentage composition ; e.g. ethyl acetate-benzene.

Type 2.—Those which exhibit definite maxima, sometimes corresponding with points of simple molecular composition. Nearly all experimental work in this class has been done on mixtures between the compounds of which chemical action might well be postulated, and the occurrence of a maximum may be regarded as pointing unmistakably to the formation of molecular complexes of a more or less stable kind.

Type 3.—Those which display a minimum point.

Seeing that the connexion between viscosity and molecular

volume is so close (cf. p. 73) these three types of mixture may be defined respectively as being composed of (1) mutually indifferent components, (2) components which undergo chemical combination to a greater or less extent, (3) associated components which bring about mutual dissociation.

Findlay [57] determined several viscosity concentration curves at the boiling-points of the individual mixtures and emphasized the fact that no simple formula could be obtained which would express the connexion between viscosity and composition. By plotting values calculated from the fluidity formula

$$\frac{1}{\eta} = \frac{v_1}{\eta_1} + \frac{v_2}{\eta_2}$$

where η_1 and η_2 refer to the viscosities of the constituents at the temperature of the experiment, and v_1 v_2 are the volumes contained in 1 c.cm. of the mixture, it was found in most cases that the observed values are smaller than those calculated by the mixture formula. The maximum deviations from the calculated values are regarded by Findlay as important, since they give an indication of the magnitude of the interaction, of whatever nature it may be, which produces divergence from the ordinary law of mixtures. A similar point of view has just been reached by Denison [58]. Bingham [59] using the data of previous workers showed that mixtures of Type 1 gave nearly linear fluidity $\left(\frac{1}{\eta}\right)$ curves, and concluded therefrom that fluidities are additive.

Mixture Formulæ.—The failure of the linear formula

$$\eta = v_1 \eta_1 + v_2 \eta_2$$

where η_1 and η_2 are the viscosities of the two components and v_1 v_2 the percentage volume concentrations has already been indicated.

The logarithmic formula of Arrhenius [60]

$$\eta = \eta_1^{v_1} . \eta_2^{v_2} \text{ or } \log \eta = v_1 \log \eta_1 + v_2 \log \eta_2$$

holds fairly well for mixtures of liquids when one component is present to the extent of 90 per cent or more, but is not valid throughout the whole range of mixtures. Lees [61], after an examination of the various formulæ, found that the fluidity formula,

$$\frac{1}{\eta} = \frac{v_1}{\eta_1} + \frac{v_2}{\eta_2}$$

is also unsatisfactory and that exact agreement can only be obtained by the introduction of a supplementary constant depending on the particular mixture considered. Jones, Bingham and McMaster [62] considered that fluidity and not viscosity is the characteristic additive property, but the calculations of Lees show that this is not the case if the concentrations are expressed as volume percentages, nor is it when they are expressed as weight percentages as urged by Drucker and Kassel.[63] Kendall [64] in view of these failures proposes a modified Arrhenius formula

$$\log \eta = \eta_1 \log \eta_1 + \eta_2 \log \eta_2$$

where η_1 η_2 are the *molecular percentage concentrations* of the two components in the mixture. The following illustrations show the applicability of the formula.

TABLE XXXIII.—Carbon Tetrachloride and Benzene, 60° C. (Thorpe and Rodger's Data).

Mols. of C_6H_6 per cent.	η Observed.	η Calculated.	Percentage Difference.
0·00	0·00582		
36·10	0·00503	0·00504	0·0
60·42	0·00456	0·00457	0·0
80·41	0·00422	0·00423	0·0
100·00	0·00391		

TABLE XXXIV.—Ethyl Acetoacetate and Pyridine at 25°. (Dunstan and Stubbs' Data.)

Mols. of Ester per cent.	η Observed.	η Calculated.	Percentage Difference.
0·00	0·008805		
11·14	0·009297	0·00934	0
22·30	0·009918	0·00992	0
38·76	0·01090	0·01085	0
59·88	0·01233	0·01215	− 1
100·00	0·01508		

Kendall also tried a molecular fluidity formula, but it gave no results superior to those cited above. These facts militate against the view which recently has been persistently set forth, that fluidity and not viscosity is the essential additive property, and they show that neither fluidity nor viscosity is the true additive

property but the logarithms of these quantities (since obviously $\frac{1}{\eta}$ may be substituted for η without affecting the result).

Viscosity Formulæ for Solutions of Solids in Liquids.—The formulæ which have been suggested to express the viscosity of solutions are, in general, similar to those for binary mixtures of liquids and are similarly unsatisfactory (Kendall, loc. cit.). Thus the linear formula

$\eta = (1 + Ax)\,\eta_0$ where η_0 is the viscosity of the pure solvent, x the volume of solute per unit volume of solution and A a constant, holds only for very dilute solutions and the same is true of Arrhenius' logarithmic expression $\eta = A^x\eta_0$ or $\log \frac{\eta}{\eta_0} = x \log A$. Green [65] found in the case of sucrose solutions that none of the current formulæ was valid over a wide range of concentration and put forward the equation

$\eta = A^{\frac{v}{w}}\,\eta_0$ where v is the volume of sucrose and w that of water in unit volume of solution. Kendall again suggested a logarithmic expression,

$$\log \frac{\eta}{\eta_0} = x \log A$$

which is the Arrhenius formula modified by substituting *molecular concentration* of solute in a fixed weight of solvent. Two illustrations of the application of this expression may be given.

TABLE XXXV.—The Octyl Hydrogen Phthalates (*r*, *d* and *l*) in Benzene at 25°. (Dunstan and Thole's Data.)

Mols. Solute in 100 Mols. Solvent.	η Observed.	η Calculated.
0·00	0·006030	
r. 1·805	0·006767	0·006787
r. 2·597	0·007189	0·007156
r. 3·363	0·007520	0·007520
r. 5·097	0·008432	0·008424
r. 5·228	0·008604	0·008498
r. 6·490	0·009190	0·009230
d. 1·910	0·006844	0·006835
d. 3·478	0·007575	0·007575
d. 3·642	0·007631	0·007657
d. 6·996	0·009525	0·009544
l. 6·928	0·009418	0·009499

TABLE XXXVI.—Sucrose in Water at 25° C. (Green's Data.)

Mols. of Sucrose per 1000 Grm. of Water.	η.	A.
0	0·008953	
0·4382	0·013083	2·38
0·9666	0·02105	2·42
1·618	0·03805	2·44
2·440	0·07973	2·45
3·516	0·2072	2·44
5·440	1·058	2·41

The constancy of the value of A shows that the formula holds satisfactorily throughout the whole range of concentration even when the viscosity of the solution is more than one hundred times greater than that of water.

Quite recently Dolezalek and Schulze,[127] investigating the system ether-chloroform, have shown that the equilibrium $C_4H_{10}O + CHCl_3 \rightleftharpoons C_4H_{10}O \,.\, CHCl_3$ is established and that the percentage amount of the compound can be calculated by the application of the law of mass action.

The viscosities of the various mixtures of ether and chloroform which vary very considerably from those calculated by the mixture law are shown to agree excellently with those calculated on the supposition that each mixture contains an amount of the compound determined by the above considerations.

Viscosity Maxima and their Interpretation.—Having dealt with the viscosity concentration curves which belong to Type 1, it is now necessary to discuss the very important cases in which maxima appear.

Based on the view that associated liquids in general, and hydroxylated liquids in particular have a relatively high viscosity coefficient, the conclusion may be drawn that a maximum point in a viscosity-concentration curve means further association proceeding in the direction of complex formation, whilst the existence of a minimum point tends to the opposite view, namely, that some dissociation has resulted.

The simple view taken by Graham [24] that the maximum point definitely indicated the existence of a compound, and, moreover, established its composition, has been generally criticized as being far too explicit. It seems probable, however, that in some cases

this view is sound, as will be seen later. Where, however, the amount of chemical affinity between the components is not sufficient entirely to bring about combination, the position of the maximum will vary within limits depending on temperature, the viscosity of the constituent liquids, and the degree of dissociation of the compound.

Washburn,[66] in a valuable summary of the theory of hydration, dealing with the deviations of property-composition curves from those demanded by the law of mixtures, agrees that striking irregularities exist, which may be quite invariant with temperature, such as the expansion-coefficient of aqueous solutions of nitric acid and sulphuric acid, which clearly indicate the existence of the hydrates HNO_3,H_2O; H_2SO_4,H_2O. Such irregularities are not found for mixtures the components of which show no chemical affinity for each other. However, Washburn sums up his review by stating that the deviations of a physical property from the mixture law cannot give any conclusive evidence regarding the existence of a hydrate (or complex). This statement is directly contrary to the views which have been held by a great number of investigators in this field (see Trans. Chem. Soc., 1909, 95, 1556).

Tsakalotos[67] has investigated maximum points on viscosity-concentration curves, and holds the opinion that the study of the viscosity curves in conjunction with the freezing-point curves proves undoubtedly that the viscosity maxima must be attributed to molecular compounds in a state of partial dissociation. The discrepancy between the compositions of the mixtures of maximum viscosity and maximum freezing-point for aniline-*m*-cresol, *p*-toluidine-*m*-cresol must be attributed to the difference existing between the viscosity of the two components and the partial dissociation of the molecular aggregate. He imagines the mixture as containing two different components, namely, (1) the inactive mixture of the original constituents, and (2) the complex aniline-phenol. Mixture (1) gives a linear mixture-law curve. The effect of (2) alone would be a maximum at 50 mols. per cent. The resultant of these curves has a maximum displaced towards the component of greater viscosity.

Faust[30] points out that it is very probable, although not absolutely proved, that in those cases where a maximum viscosity occurs a chemical compound is produced. Thus there is always

such a maximum when the components are an acid and a base. In all cases where there is an evolution of heat on mixing, the compounds will dissociate with rising temperature, and so the viscosity curve will reproduce the dissociation by showing a smaller and smaller deviation, and at high temperatures will approach linearity. It is, however, untrustworthy to deduce from the position of the maximum the chemical composition of the compound, since the position frequently alters with temperature, and depends on the relative viscosities of the two components. On the other hand, when the viscosity curve is sagged, it must be interpreted as a result of dissociation (compare Dunstan [56]). Faust also noticed that maxima on viscosity curves correspond with minima on vapour-pressure curves, a fact which is compatible with the formation of a molecular compound.

Denison [58] considers that the formation of a maximum does imply molecular aggregation, but prefers to determine the nature of the complex by the maximum deviation from the mixture law rather than from the position of the maximum itself. It should be mentioned that other observers, notably Findlay [57] have emphasized the fact that the greatest deviation should be considered, and not the actual maximum. Denison assumes that where complex formation is possible, there will be a solution of the complex in a mixture of the unaltered components. This mixture of complex and unchanged components will tend to form a maximum at some point along the curve, depending on its relative viscosity. It follows as a corollary that if most or all of the components associate in this way, the maximum point must agree with the composition of the complex. As Baker [68] has indicated, however, the complex may be of less viscosity than one or other of the components (assumed to be very associated), in which case a sagged curve or a minimum might be obtained. Baker, in fact, draws the conclusion that in mixtures of alcohol-ether, used for dissolving nitrocellulose, there is a complex existing, but the shape of the curve does not in any way indicate it.

On surveying these various opinions, it will be evident that they conform to the belief that a maximum viscosity does indicate some molecular aggregation, but the mass of evidence is decidedly against any predication that the position of the maximum point may indicate the composition of the compound.

It will be obvious that this position can be influenced by a variety of causes. Suppose two liquids, A and B, the association factors of which are n and m, tend on mixing to form the compound AB. Then

$$A_n + B_m \rightleftharpoons (n - x)\,A + (m - x)\,B + xAB,$$

where x is the amount of AB present.

Four cases present themselves:—

Case 1.—x is very small, and A_n and B_m are stable, and have little mutual action. A linear or slightly sagged curve will result; for example, phenol—α-naphthylamine.

Case 2.—x is fairly large, there is considerable chemical affinity, and the complexes A_n and B_m are mutually fairly stable. Then if the viscosity of the complex AB is less than that of one or other of the components, there will be a sagged curve; for example, phenol-acetone, lactic acid-water.

Case 3.—x is fairly large, there is considerable chemical affinity, and the viscosity of the complex is greater than that of A_n and B_m, which are mutually somewhat unstable. Then there will be a maximum point, but its position will depend on temperature and the relative viscosities of A_n, B_m, and AB; for example, alcohol-water.

Case 4.—x is very large, and chemical action very considerable; the complexes A_n and B_m are dissociated. Then there will be a definite maximum corresponding with the actual molecular concentration of A and B in AB; for example, sulphuric acid-water.

It has been found that in the large majority of cases a maximum in the melting-point curve means a maximum in the viscosity curve as will be evident from the following table.

TABLE XXXVII.—Liquid Mixtures which show Maximum Points.

Mixture.	Maximum.	Observer.	Fusion Curve.
Water – methyl alcohol	Approximately $MeOH, 3H_2O$	Getman, Dunstan	—
Water – ethyl alcohol	Approximately $EtOH, 3H_2O$	Poiseuille, Graham, Dunstan, Traube	—
Water – propyl alcohol	Approximately $PrOH, 2H_2O$	Dunstan	
Water – acetic acid	$CH_3 \cdot CO_2H, H_2O$	Graham, Dunstan, Wijkander	No maximum, Kremann, "Sitzungsber. K. Akad. Wien," 1907, **116**, 795
Water – propionic acid	Approximately $C_2H_5 \cdot CO_2H, H_2O$	Tsakalotos	
Water – pyridine	Approximately $2C_5H_5N, 5H_2O$	Hartley, Thomas and Applebey [69]	
	Approximately 30 mols. per cent pyridine	Dunstan and Faust	
Water – sulphuric acid	H_2SO_4, H_2O	Graham, Knietsch,[70] Dunstan, Kremann and Ehrlich	Maximum, $H_2SO_4 \cdot H_2O$, Knietsch, Kremann
Sulphuric acid – sulphur trioxide	H_2SO_4, SO_3	Dunstan and Wilson	Knietsch, maximum
Aniline – *m*-cresol	Approximately 2 *m*-cresol : 1 aniline	Tsakalotos	Maximum, Kremann, "Sitzungsber. K. Akad. Wien," 1905, **112**, 1201.
o-Toluidine – *m*-cresol	Approximately 4 *m*-cresol : 1 toluidine	Tsakalotos	Kremann, loc. cit.
Acetone – chloroform	Approximately 4 chloroform : 1 acetone at 0°	Tsakalotos	
	and 3 chloroform : 1 acetone at 13°	Faust	
	No maximum at 19°	Faust	
Pyridine – acetic acid	Approximately 4 acetic acid : 1 pyridine	Tsakalotos	
	Approximately 4 acetic acid : 1 pyridine	Faust	
	Very slight shift of maximum between 0° and 99°	Faust	
Pyridine – butyric acid	Approximately 4 butyric acid : 1 pyridine	Tsakalotos	
Aniline – acetic acid	Approximately 2 acetic acid : 1 aniline at 18°—60°	Faust, Thole, Dunstan and Mussell [72]	
Acetic anhydride – water	Approximately 2 water : 1 anhydride, invariant between 0° and 73°	Faust	
Iso-butyric acid – water	Approximately 3 water : 1 acid	Tsakalotos	

TABLE XXXVII.—Liquid Mixtures which show Maximum Points—(*Cont.*).

Mixture.	Maximum.	Observer.	Fusion Curve.
n-Butyric acid – water	Approximately 2 water : 1 acid	Tsakalotos	
Triethylamine – water	Approximately 5 water : 1 amine	Tsakalotos	
Nicotine-water	Approximately 3 water : 1 amine	Tsakalotos	
Allyl thiocarbimide – piperidine	Exactly 1 amine : 1 thiocarbimide	Kurnakov and Schemtschushni [71]	
Phenyl thiocarbimide – diethylamine	Exactly 1 amine : 1 thiocarbimide	,,	
Allyl thiocarbimide – methylaniline	Exactly 1 amine : 1 thiocarbimide	,,	
Ethyl thiocarbimide – piperidine	Exactly 1 amine : 1 thiocarbimide	,,	
Aniline – *o*-chloro-phenol	Nearly 1 amine : 1 phenol	Thole, Dunstan and Mussell	
Aniline – *m*-chloro-phenol	Approximately 1 amine : 1 phenol	,,	
Aniline – *p*-chloro-phenol	20 per cent aniline	,,	
Phenyl hydrazine – phenol	1 base : 1 phenol exactly	,,	Ciusa and Bernardi "Gazzetta," 49, 1, 159, 1910, maximum at 1 base : 1 phenol
Phenyl hydrazine – *o*-chlorophenol	1 base : 1 phenol exactly	,,	
Chloral – water	1 : 1 nearly	Kurnakov and Efremov [126]	
Chloral – alcohol	1 : 1 nearly	,,	
p-Cresol – aniline	Indefinite	Thole, Dunstan and Mussell	Maximum at 1 amine : 1 phenol, Philip, "Trans., Chem. Soc.," 1903, 183, 814
Phenol – *p*-toluidine	Approximately 1 amine : 1 phenol	,,	,,
α-Naphthylamine – phenol	Indefinite	,,	,,
Aniline – phenol	Indefinite	,,	Maximum at 1 amine : 1 phenol, Schreinemakers, "Zeits. Physikal. Chem.," 1899, 31, 581

It will be noticed from the above table that in some cases the evidence of the fusion curves is closely paralleled by that of the viscosity curves, for example, for sulphuric acid-water, *o*-chlorophenol-aniline, phenol-phenylhydrazine, aniline-phenol, *o*-chlorophenol-phenylhydrazine. In the majority of maxima, however, there is a distinct shift from the point of equimolecular concentration. One must therefore incline to the view that the appear-

ance of a maximum on a viscosity concentration curve does indicate the existence of chemical combination between the components, but the position depends on several independent factors, namely, the actual viscosity of the components (which is intimately connected with their degree of association), and the degree of dissociation of the compound itself at the temperature of observation. It by no means follows that the absence of a maximum point precludes complex formation, as, indeed, has

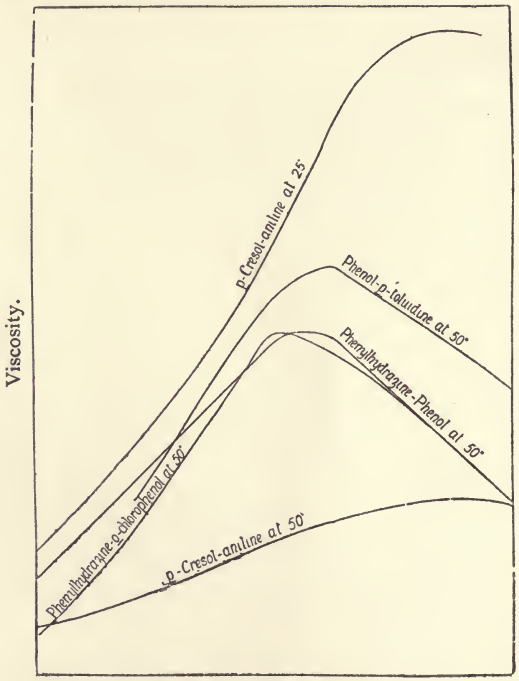


FIG. 5.—Percentage Composition.

been pointed out repeatedly; for obviously the viscosity of one highly associated component may be greater than that of the complex (see also Baker, loc. cit.). Comparison of the viscosity with the fusion curves and with the vapour pressure curves is valuable, for, as Faust has indicated, there is a close connexion between vapour pressure and viscosity, since whatever forces operate in complex building would similarly depress the vapour pressure.

A few curves where viscosity maxima are to be observed are shown in Fig. 5.

A very striking confirmation of the validity of the above views has been obtained by Kurnakov and Schemtschushni.[71] These authors have investigated at various temperatures the viscosity concentration curves of irreversible binary systems where liquid and completely miscible compounds are formed. The viscosity isotherms consist of two separate branches convex to the composition axis intersecting at an angle (increasing in acuteness as the temperature is lowered), and this maximum point occurs at exactly equimolecular concentration.

CHAPTER VI.

VISCOSITY OF ELECTROLYTIC SOLUTIONS.

THE viscosity of salt solutions naturally attracted the attention of the earlier workers, and so far back as 1873 Hübner [73] determined the viscosities of a series of solutions of alkaline haloids of equal density and found that some of the salts diminished the viscosity of water, whilst Sprung [74] discovered that his experimental material fell into two classes:—

(1) KCl, KBr, KI, KNO_3, $KClO_3$, NH_4Cl, NH_4Br, NH_4NO_3; (2) K_2SO_4, NaCl, NaBr, NaI, $NaNO_3$, NaClO, Na_2SO_4, $(NH_4)_2SO_4$, $BaCl_2$, $SrCl_2$, $CaCl_2$, LiCl, $MgSO_4$.

At low temperatures the salts in the first group depress the viscosity of water and at high temperatures they increase it, whilst salts of the second group always increase the viscosity of the solvent. Slotte,[75] Arrhenius,[60] Wagner,[76] Ranken and Taylor [77] and Getman [78] have also experimented in this direction. The last mentioned considers that the "negative viscosity" shown by salts of the first class is due to the specific effect of the potassium and ammonium ion, since the undissociated molecule (and the anions) bring about an increase in viscosity. This view is shared by Jones and Veazey [79] who state that cations of large ionic volume diminish the viscosity of water.

It is obvious that one must consider not only the amounts of the ions and the undissociated salt present but also the degree of hydration of each of these components and further the effect of the salt and of its ions on the molecular complexity of the solvent. Further it must be remembered that all these quantities vary with temperature and concentration. It is not surprising, therefore, that little progress has been made in the direction of finding a quantitative expression which will represent the viscosity of a salt solution.

Viscosity and Conductivity.—As early as 1856 Wiedemann [80] drew attention to the fact that viscosity and conductivity are

closely related and showed that $\frac{K\eta}{m}$ = constant, where K is the conductivity of the solution whose concentration is m, and similar empirical relationships have been pointed out by Grotian,[81] Grossmann,[82] Arrhenius [83] and Kohlrausch.[84]

To illustrate the nature of this connexion the following results obtained by Getman [78] may be quoted.

TABLE XXXVIII.—Equivalent Conductivity and Viscosity at 18°.

Salt.	η.	Λ.	$\eta\Lambda$.
NaCl	0·0116	74·4	·863
NaBr	0·0115	70·5	·811
$NaNO_3$	0·0114	66·0	·752
KCl	0·0105	98·2	1·031
KBr	0·0103	103·7	1·069
KI	0·0101	103·4	1·041
KNO_3	0·0104	80·4	·839
NH_4Cl	0 0103	97·0	·999
NH_4Br	0·0101	102·9	1·039
NH_4I	0·0098	104·0	1·016
NH_4NO_3	0·0101	88·9	.901

It is evident that some other factor besides those given is required to establish the relation between viscosity and conductivity.

It has been shown by Bousfield [85] that the application of Stokes' theory respecting the limiting velocity of a small sphere moving under a constant force in a viscous medium is of great value in studying the various causes which may affect the mobility of an ion. The limiting velocity of a sphere of radius r, moving in a medium of viscosity η, under a constant force p is proportional to $\frac{p}{r \cdot \eta}$. Applying this to the case of an ion moving with a spherical solvent atmosphere around it, the mobility of the ion will depend on the viscosity of the solution and on the size of the envelope.

Hartley, Thomas and Applebey [86] employed Stokes' theory in connexion with the conductivity of lithium nitrate dissolved in various aqueous pyridine solutions (Figs. 6 and 7). Assuming that U_A and U_C are the absolute velocities of anion and cation at infinite dilution under unit gradient, r_a and r_c the radii of the ions

$$U_A = C\frac{I}{r^a\eta} \text{ and } U_C = C\frac{I}{r^c\eta}$$

and since $\Lambda_\infty = Q\,(U_A + U_C)$, Q being the charge liberated by 1 gram equivalent of a univalent ion,

$$\Lambda_\infty = \frac{Qc}{\eta}\left(\frac{I}{r_a} + \frac{I}{r_c}\right).$$

It follows then that any variation in $\Lambda_\infty \eta$ indicates a

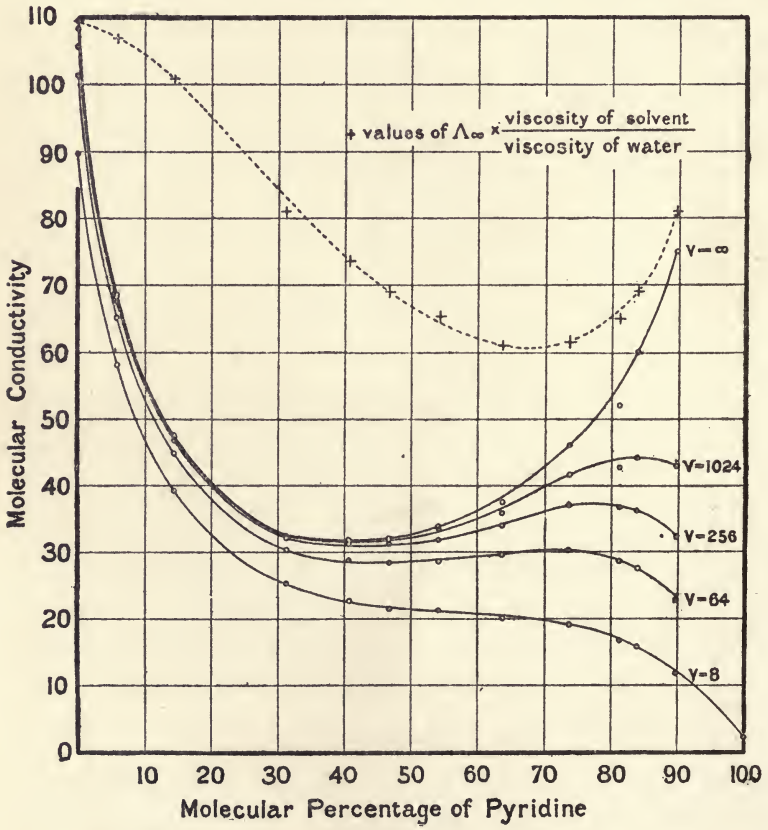


FIG. 6.

change in the size of the solvent envelope attached to the ions. The following table shows that as the amount of pyridine is increased the ion atmospheres increase till the solution contains about 67 mols. per cent of pyridine and then steadily become less.

TABLE XXXIX.—Effect of Pyridine on Size of Solvent Atmosphere.

Mols. per cent Pyridine.	Λ_∞.	η.	$\Lambda_\infty \cdot \frac{\eta \text{ (Solvent)}}{\eta \text{ (Water)}}$.
0·00	57·10	0·01778	57·1
14·47	19·05	0·04735	50·7
40·64	13·40	0·04990	37·6
54·35	16·25	0·03625	33·1
73·76	27·5	0·02055	32·0
83·98	39·0	0·01645	36·0

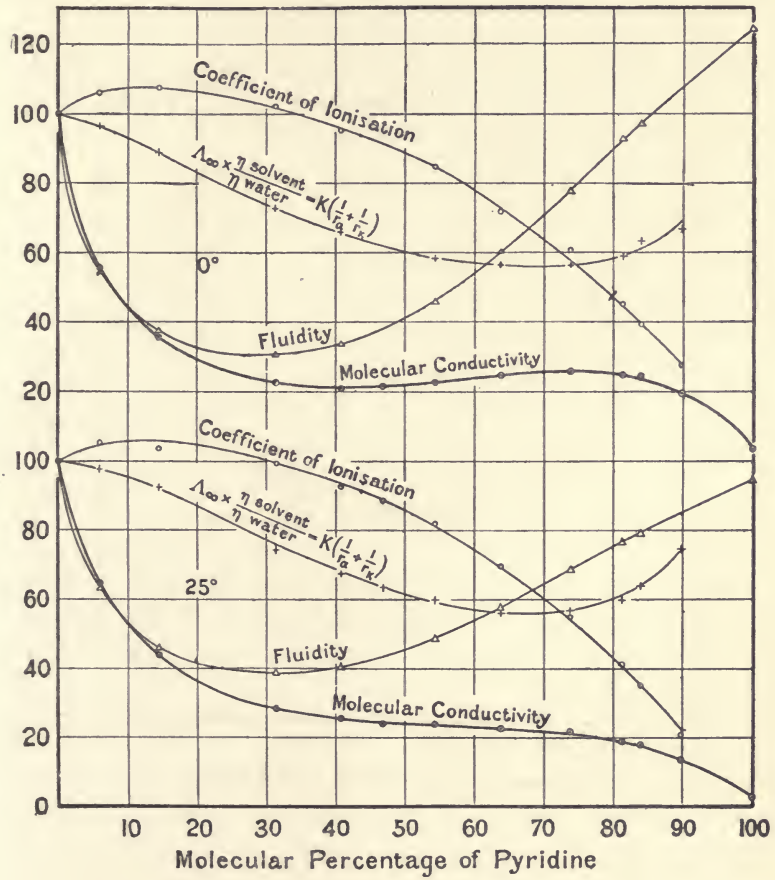


Fig. 7.

The ordinary equation used in calculating coefficients of ionization, namely, $a = \frac{\Lambda_v}{\Lambda_\infty}$ neglects changes in the mobilities of the ions at different concentrations due to changes in the viscosity of the solution and to variations in the size of the solvent atmosphere attached to them. Hartley and his co-workers point out (loc. cit.) that on the assumption that the mobility of the ion varies inversely with the viscosity of the medium (see Bousfield and Lowry [87])

$$a = \frac{\Lambda_v}{\Lambda_\infty} \times \frac{\text{viscosity of solution}}{\text{viscosity of solvent}}.$$

Heber Green,[88] however, using sucrose to increase the viscosity of the solvent, finds that Λ does not vary directly as the fluidity, but as some function more nearly approximating to $\phi^{\frac{2}{3}}$ as is shown in the following table.

TABLE XL.—Conductivities of Mixtures of Sucrose and Lithium Extrapolated to the Ratio $\frac{LiCl}{Sucrose} = \frac{N}{n} = 0$.

Mols. of Sucrose N.	$\Lambda \times 10^3$.	$\Lambda/\phi \times 10^3$.	$\Lambda/\phi^{0.7} \times 10^3$.
0	114·0	—	—
0·05	108·8	1·017	4·132
0·2	95·8	1·025	4·000
0·6	68·7	1·125	3·862
1·0	46·6	1·298	3·802
1·4	29·5	1·588	3·815
1·8	16·8	2·099	3·920

Green expresses doubt not only as to the applicability of Stokes' theory in a case where the moving body is of the same order of dimensions as the particles of the medium but also with reference to the need for assuming the existence of an aqueous envelope around each ion. He considers that the calculation of the ionization coefficient can be made in the following way.

Comparing the conductivity Λ of a pure lithium chloride solution with that Λ_f of a solution infinitely dilute with respect to lithium chloride but containing enough sucrose to give it the same fluidity as the first solution, then the coefficient of ionization will be

$$x = \frac{\Lambda}{\Lambda_f}.$$

TABLE XLI.—Ionization Coefficients for Solutions of Mixtures of Lithium Chloride and Sucrose. Ratio $\frac{Mols.\ of\ LiCl}{Mols.\ of\ Sucrose} = 5{\cdot}0$.

f.	$\Lambda \times 10$.	$x = \Lambda/\Lambda f$.
111·7	—	1·000
111·26	1·070	0·944
110·30	1·016	0·904
109·45	0·9009	0·885
89·13	0·8045	0·7795
44·84	0·3875	0·710
18·51	0·19105	0·649
5·121	0·0722	0·578

These figures for x are not to be regarded as true ionization factors since the ionic mobilities in solutions of the same fluidity will vary according as the viscosity is mainly due to lithium salt, sucrose, or other added substances (see also Washburn [92] who developed a similar formula $\Lambda = K\phi^m$, m being not far removed from unity).

This conclusion becomes additionally interesting from the fact that similar considerations apply to the relationship between the fluidity and ionic mobility of aqueous solutions when these are modified continuously by changing the temperature instead of by the addition of a foreign substance. From the work of Noyes and his colleagues, Johnston [128] has deduced the following values for a series of ions from the relationship $\mu_\infty = K^n\phi^n$.

	K.	Na.	NH_4.	Ag.	½Ba.	½Ca.
n	0·887	0·97	0·891	0·949	0·986	1·008
log K	+0·054	−0·281	+0·045	−0·143	−0·212	−0·286
μ_∞ for 0°	40·4	26	40·2	32·9	33	30

	Cl.	NO_3.	$C_2H_3O_2$.	¼FeC_6N_6.
n	0·88	0·807	1·008	0·929
log K	+0·074	+0·194	−0·455	+0·139
μ_∞ for 0°	41·1	40·4	20·3	58

It will be noticed that the more mobile of the ions are those that show the greatest deviation from the linear law, the index n being less than 1 in each case. The less mobile ions give an index very near to unity with an almost exact proportionality between mobility and fluidity.

The subject was developed still further by Applebey [89] who continued the work of Grüneisen and extended it considerably. Grüneisen had shown that the viscosity concentration curves for all dilute salt solutions exhibit a remarkable change of curvature

in the sense that the first portions of salt added to water have a greater effect in increasing or a less effect in diminishing the viscosity than subsequent additions. This effect is most clearly shown when one plots $\frac{\text{relative viscosity} - 1}{\text{mol. concentration}}$ against cube root of concentration (Fig. 8).

No such effect as this has ever been observed with non-electrolytes, and it is not surprising therefore that Grüneisen en-

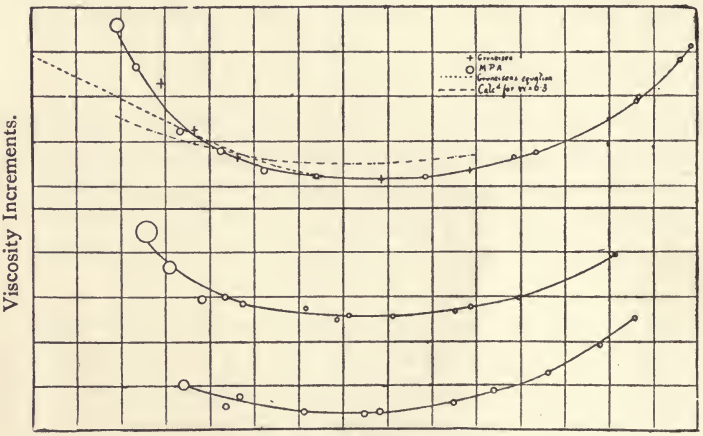


FIG. 8.—10 × $\sqrt[3]{\text{Concentration}}$.

deavoured to connect the phenomenon with ionization. The following formula was found to reproduce the observations with a fair degree of accuracy:—

$$\frac{\frac{\eta}{\eta_0} - 1}{m} = A\alpha + B(1 - \alpha) + Cm$$

where η/η_0 = the relative viscosity; m = molecular concentration; α = degree of ionization and A, B, C are constants.

A series of results for lithium nitrate obtained by Applebey is given on opposite page.

Applebey found that the results for the very dilute solutions departed somewhat from those calculated by Grüneisen's formula and this divergence is apparent in figure 8, where the calculated values are shown by a dotted line. Now Grüneisen's equation contains the assumption that the effects of the ion and of undissociated salt respectively are distinct and separable and that each is in all cases proportional to the concentration of the component

TABLE XLII.—Viscosity of Lithium Nitrate Solutions.

Concentration (m).	$10m^{1/3}$	$\frac{\eta}{\eta_0}$.	$\frac{\eta/\eta_0 - 1}{m}$.
0·0174	2·59	1·0026	0·149
0·0567	3·84	1·0067	0·119
0·1071	4·75	1·0125	0·1165
0·3643	7·142	1·0405	0·1111
0·8666	9·533	1·0980	0·1131
1·316	10·96	1·1567	0·1191
3·8541	15·678	1·74075	0·1922
4·578	16·60	2·0577	0·2310
5·849	18·02	3·0255	0·346

considered. This can be true only if the process of solution is merely a mechanical mixing, and if the view, generally accepted now, that the act of solution interferes with the molecular complexity of the solvent is to be rejected.

On the assumption that the viscosity is proportional to the mean molecular volume and that the different molecular species present in a salt solution are: (*a*) simple water molecules, H_2O; (*b*) associated water molecules assumed to be triple, $(H_2O)_3$; (*c*) ions, hydrated to an unknown extent, $Li \,.\, xH_2O$, $NO'_3 \,.\, yH_2O$; (*d*) undissociated molecules, possibly combined with water, $LiNO_3$; (*e*) salt complexes in strong solutions, $(LiNO_3)_n$, Applebey deduces the formula

$$\frac{\eta}{\eta_0} = \frac{c'_1 + c'_3}{c_1 + c_3 + ms\,(1 + a)}$$

where c_1 is the concentration of single H_2O molecules, c_3 the concentrations of triple molecules in the solution, c'_1 and c'_3 the respective concentrations in pure water, m the weight normality, s the density, and a the degree of ionization.

Using Kohlrausch and Mailey's [90] conductivity determinations to find a from the relation $a = \frac{\Lambda}{\Lambda_\infty} \times \frac{\eta}{\eta_0}$, it may be shown that an approximate value of the degree of hydration of lithium nitrate is determinable.

Unfortunately, however, Applebey's formula cannot at present be submitted to a quantitative test; but there is no doubt that a formula of this kind will have to be taken into account when sufficiently accurate determinations of the variables involved are available.

In an investigation of the viscosity of caesium nitrate solutions Merton,[91] following the procedure of Applebey, found that at all temperatures the viscosity of these solutions is less than that of water, and confirmed Grüneisen's discovery anent the change of curvature at the dilute end of the viscosity-concentration curve. Qualitatively, viscosity changes follow the classification of the elements in the periodic system and so, seeing that the caesium ion in aqueous solution is the smallest of its group, it possesses the largest ionic mobility.

On surveying the behaviour of aqueous electrolytic solutions outlined above it will be obvious that the whole problem is complicated by the anomalous behaviour of water, and that simple relationships might be expected from an organic solvent. This aspect of the question has been successfully attacked by Walden[93] who has used such salts as tetramethyl ammonium iodide, and sodium iodide dissolved in a variety of organic liquids. In all cases, no matter what the solvent may be, it appears that at infinite dilution the relationship

$$\Lambda_\infty \eta_\infty = \text{constant}$$

is very nearly correct. The following numbers, obtained by Walden, may be quoted in support of this.

TABLE XLIII.—Solutions of Tetra Methyl Ammonium Iodide at 0° C. and 25° C.

Solvent.	$\Lambda_\infty \eta_\infty$ at 0° C.	$\Lambda_\infty \eta_\infty$ at 25° C.
Acetone	0·703	0·711
Propionitrile	0·618	0·682
Nitromethane	0·775	0·743
Methyl alcohol	0·761	0·719
Ethyl *iso*-thiocyanate	0·694	0·655
Methyl *iso*-thiocyanate	0·707	0·690
Acetyl acetone	0·656	0·640
Sym, ethyl sulphite	0·655	—
Acetic anhydride	0·683	0·654
Epichlorhydrin	0·674	0·688
Ethyl alcohol	0·662	0·648
Benzonitrile	0·679	0·706
Furfurol	0·744	0·745
Diethyl sulphate	0·686	0·688
Dimethyl sulphate	0·756	0·757
	0·700	·700

TABLE XLIV.—Solutions of Tetra Propyl Ammonium Iodide at 25° C.

Solvent.	$\Lambda_\infty \eta_\infty$.
Acetone	0·632
Propionitrile	0·620
Ethylene chloride	0·615
Epichlorhydrin	0·611
Benzonitrile	0·636
Acetoacetic ester	0·616
Nitrobenzene	0·637
Benzyl cyanide	0·614
Iso-butyl alcohol	0·616
m-Chloraniline	0·635
	0·624

TABLE XLV.—Solutions of Potassium Iodide at Various Temperatures.

Solvent.	t.	$\Lambda_\infty \eta_\infty$.
Methyl alcohol	25°	0·647
Ethyl alcohol	0°	0·630
,, ,,	18°	0·616
,, ,,	25°	0·636
Acetone	0°	0·652
,,	25°	0·647
Acetonitrile	0°	0·676
,,	25°	0·693
Pyridine	0°	0·630
,,	25°	0·639
		0·650

These numbers also show that the relationship $\Lambda_\infty \eta_\infty = K$ holds good at different temperatures, e.g. the value of K for tetramethyl ammonium iodide is 700 both at 0°C and 25°C.

We may therefore write $\eta^t_\infty \Lambda^t_\infty = \eta^{t'}_\infty \Lambda^{t'}_\infty = K$

$$\text{or } \frac{\eta^t_\infty}{\Lambda^t_\infty} = \frac{\Lambda^{t'}_\infty}{\eta^{t'}_\infty}.$$

Results for water, formamide and lactonitrile are uniformly high, and so are their association coefficients and dielectric constants. It is probable, therefore, that a knowledge of these last two factors and the way in which they vary will be necessary before the behaviour of aqueous solutions is rendered intelligible.

To illustrate the result of considering dielectric constant and association factor, the following table may be consulted (Walden[94]).

TABLE XLVI.—KCl IN WATER.

	$t = 0°$.	$t = 50°$.	$t = 100°$.
Λ_∞	81·4	232·5	414
η_∞	0·0178	0·00548	0·00283
$\Lambda_\infty \eta_\infty$	1·449	1·271	1·173
Association factor (x) . .	2·52	2·24	1·98
$\frac{\Lambda_\infty \eta_\infty}{x}$	0·575	0·568	0·592
Dielectric constant ϵ . . .	87·33	70·0	56·5
$\Lambda_\infty \eta_\infty \frac{x}{\epsilon}$	0·0418	0·0407	0·0411

The validity of Walden's rule has been questioned by Dutoit and Duperthius [129] who, after making measurements of viscosity from 0° to 40° or 80° found that the magnitude of the quantity $\eta_\infty \Lambda_\infty$ was affected by change of temperature even when all the other conditions were kept constant. Thus, for solutions of sodium iodide in pyridine the product varied from 0·573 at 0° to 0·559 at 80° and in *iso*-amyl alcohol to an even larger extent, from 0·374 to 0·225. Schmidt and Jones [130] also call attention to similar discrepancies in the case of potassium iodide dissolved in methyl alcohol, ethylene glycol and glycerol.

CHAPTER VII.

THE VISCOSITY OF COLLOIDS.

Historical.—In previous chapters viscosity has been dealt with only as applied to homogeneous liquids, i.e. to one phase systems. It is obvious that an entirely different state of affairs will hold for two phase or colloidal systems. Considering first of all the case of the suspensoid where particles of extremely small size are suspended in a homogeneous medium, it has been found that the presence of the suspended particles affects but slightly the viscosity of the dispersion medium. Bingham [118] for instance, working with suspensions of china clay, graphite, and infusorial earth, concludes that the decrease in fluidity is directly proportional to the volume concentration of the suspended solid, i.e. it is very small. Much work in this field has been carried out in connexion with the so-called critical solution phenomena which manifest themselves when solutions of partially miscible liquids become heterogeneous on alteration of temperature. For instance Friedländer [112] found a marked increase in the viscosity of *iso*-butyric acid-water mixtures as the solution was cooled to the temperature where opalescence became evident and the critical solution point approached. He extended his work to aqueous solutions of phenol and the ternary system benzene-water-acetic acid, and concluded that the increase in viscosity was due to the formation of drops. Bose [111] and his co-workers have also found that abnormally high viscosities are to be found at the critical solution temperatures, and consider that this may be due to the rolling of drops in the capillary of the viscometer. They also discovered that similar abnormalities occur in the case of anisotropic liquids and regarded these "liquid crystals" as emulsions of very long life. It was pointed out that the formation of orderly oriented "swarms" of the crystalline liquid molecules would cause an increase in viscosity and Bose proposed to test this by determin-

ing the viscosity under the conditions for turbulent flow, which might conceivably break up the "swarms". Something of this sort apparently happened, for the abnormalities certainly decreased as the transpiration velocity increased.

With regard to true colloidal solutions (emulsoids) Griffiths [110] found that gelatine sols containing sodium chloride had a conductivity greater than that of a gelatine-free solution but a viscosity enormously greater, whilst Garrett [109] determined the viscosity of colloidal solutions by means of an oscillating disc and discovered that the logarithmic decrements of the amplitude of vibration increased, two facts which are explicable on the assumption that the emulsoids possess a definite structure.

Von Schroeder [108] used the viscosity method for studying the behaviour of gelatine solutions and found that the viscosity of a given solution at a given temperature was not constant but depended largely on the previous history of the system. The observed phenomena were accounted for by the overlapping of two processes:—

(1) An irreversible change, probably a chemical reaction, between the gelatine and water.

(2) The reversible change hydrosol $\rightleftarrows$ hydrogel.

The speed of the first reaction was measured by heating a gelatine solution to 100° C. for varying periods. The rate of change of viscosity is expressed by

$$\frac{d\eta}{dt} = K(\eta - \eta_f)$$ where η_f is the final value of the viscosity.

Von Schroeder calls this the "saponification reaction" since it is analogous to the hydrolysis of cane sugar.

Acids and bases accelerate the change, whilst salts are without influence. With regard to the reversible reaction a fall in temperature favours the gel formation but the change takes place slowly. Rise of temperature favours the sol formation but is accompanied by hydrolysis of the gelatine, so that if the solution is heated till the sol is completely "saponified" then on cooling no gel is formed and the viscosity remains constant.

The Viscometer as Colloidoscope.[1]—In a general introduction to the subject of colloids and their viscosity Wo. Ostwald [107] draws particular attention to the enormous qualitative and quan-

[1] The material in this section has been largely taken from the recent "General Discussion on Colloids and their Viscosity," "Trans. Faraday Society," 1913, 9, 34.

titative variability of the viscosity of substances in the colloidal state. Whereas the viscosity of a molecular solution is defined completely by the concentration and the temperature, that of a colloid presents an entirely different problem. In the simplest case, viz. a suspensoid colloid in which the disperse phase still retains the properties of the solid state, one further variable must be considered, the size of the particles or degree of dispersity.

A greater number of variables defines the viscosity of the emulsoid colloids, where not only *concentration, temperature* and *degree of dispersity* must be taken into account but also

(1) *solvate formation.*—The viscosity increases with the amount of dispersion medium taken up by the disperse phase.

(2) *Electric Charge.*—Ionized particles which move in the electric field impart to the system a materially greater viscosity than uncharged particles.

(3) *Previous Thermal Treatment.*—A gelatine sol which has been repeatedly warmed and cooled has, at first, a lower viscosity at the same temperature than a similar sol which has not been so treated.

(4) *Previous Mechanical Treatment.*—A decrease in the viscosity of gelatine sols can be produced by repeatedly forcing the same liquid through the viscometer.

(5) *Inoculation with Small Quantities of more Viscous Colloids.*—Small additions of more viscous colloids after some time raise the viscosity of gelatine solutions to an incomparably higher extent than would correspond with the increase in concentration due to the addition.

(6) *Time.*—The time factor has perhaps the most striking effect on the viscosity of hydrated colloids. In all determinations of the viscosity of such colloids different values are obtained according to the age of the sol, and according to the velocity with which the temperature is being altered. The age-viscosity curve appears generally to be S shaped.

(7) *Addition of Electrolytes and Non-electrolytes.*—Most varied effects are produced by relatively small additions of substances.

It is particularly remarkable that relatively enormous changes of viscosity occur within very narrow limits of temperature and concentration. A gelatine sol may, by merely altering these variables or even by mere ageing, pass through all values of

viscosity from that of water to that of a solid. Soap sols can attain the viscosities of solids at concentrations less than 1 per cent.

Viscosity as a Methodic Principle.—If it is desired to follow quantitatively the alterations of dispersity or of solvate formation, such as coagulation, peptonization, gelatinization and so on, any physico-chemical property of the system may be used as an indicator of such changes. In practice that property will be chosen which shows the largest possible variation with small

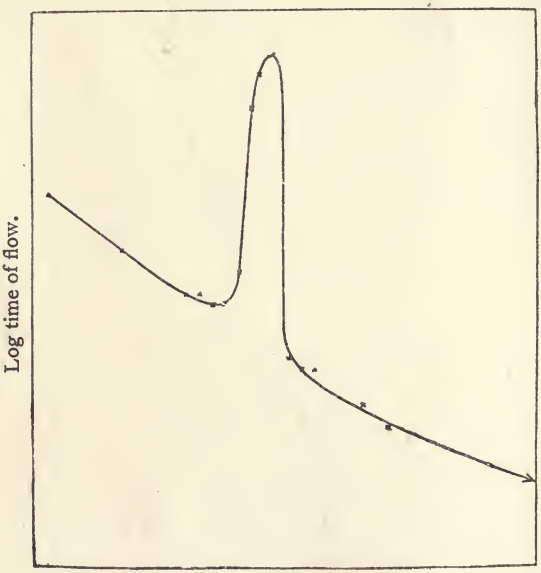


FIG. 9.

changes in the colloidal condition and which lends itself to convenient measurement. These requirements are eminently fulfilled by viscosity.

As an illustration of the application of the viscosity method may be quoted the change undergone by a dilute albumen sol on heating.

Fig. 9 shows the viscosity changes, with temperatures as abscissæ and logarithms of times of flow as ordinates. Between 50° and 57° the viscosity decreases in the normal manner. At 57·5°, shortly before the appearance of turbidity, a large increase in viscosity takes place which at 60° gives place to an equally

steep decrease. After that the viscosity curve of the coagulated albumen proceeds practically in the original direction as if nothing had happened.

Another interesting case is the viscosimetric behaviour of a starch suspension during heating, a process which leads to the well-known gelatinization (Fig. 10). At first the viscosity falls in the normal way and then extremely rapidly at 57° a sharp

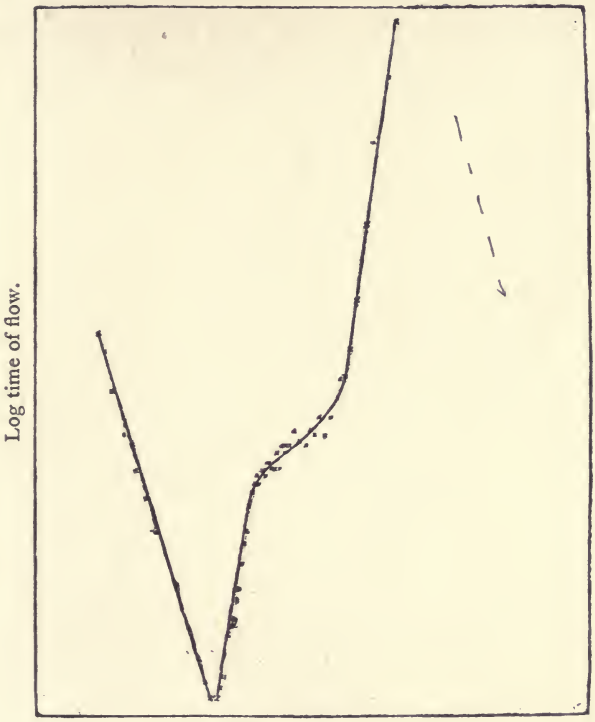


FIG. 10.

break occurs and the curve rises sharply to 65°, then bends away and again rises to 95°.

Viscosity and Continuity.—Modern colloidal chemistry has led to the discovery that continuous transitions are possible between coarse suspensions, colloidal solutions, and systems of molecular dispersity. A number of transitional systems on the border of colloidal and molecular dispersity may be mentioned which show pronounced anomalies of viscosity. First may be instanced the critical mixtures of liquids, e.g. isobutyric acid and

water at certain temperatures and concentrations (Fig. 11). Then the percentage increase in viscosity of a critical water isobutyric acid mixture containing 38·6 per cent of acid amounts to 34·3 per cent per degree. Other systems exhibiting entirely analogous anomalies of viscosity are, for instance, liquid sulphur above 130° and the opalescent liquid crystals ; and in these cases very great temperature coefficients of viscosity are met with. On cooling molten sulphur from 400° to 200° the viscosity rises from 150 to 50,000 and falls to 8 at 150° (Fig. 12). Wo. Ostwald (loc. cit.) justly

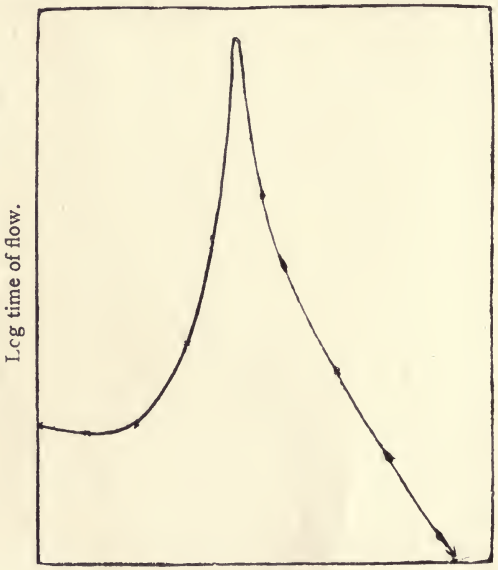


FIG. 11.

points out that the remarkable similarity between the cases just mentioned and purely colloidal phenomena such as the gelatinization of starch can only be explained by the theory that colloids, critical mixtures, crystalline liquids, melted sulphur, etc., are all disperse systems, i.e. systems whose properties are periodically discontinuous in space, this period being extraordinarily small. In other words this theory applies not only to coarsely heterogeneous systems but also to purely molecular systems.

Hatschek's Work.—Apparently the only successful attempt to find a mathematical expression for the viscosity of a two phases system is due to Hatschek[115] who deduced the equation

$$\eta_1 = \eta(1 + 4{\cdot}5f)$$

where η_1 is the viscosity of the system, η that of the liquid continuous phase and

$$f \text{ is the ratio } \frac{\text{total volume of disperse phase}}{\text{total volume of system}}.$$

Einstein [106] obtained a similar expression, viz. $\eta_1 = \eta(1 + f)$.

These formulæ state that the viscosity of a system of deformable particles suspended in a liquid is independent of the size of the particles and is a linear function of the volume of the disperse phase only. Whilst Hatschek's formula has been found to hold

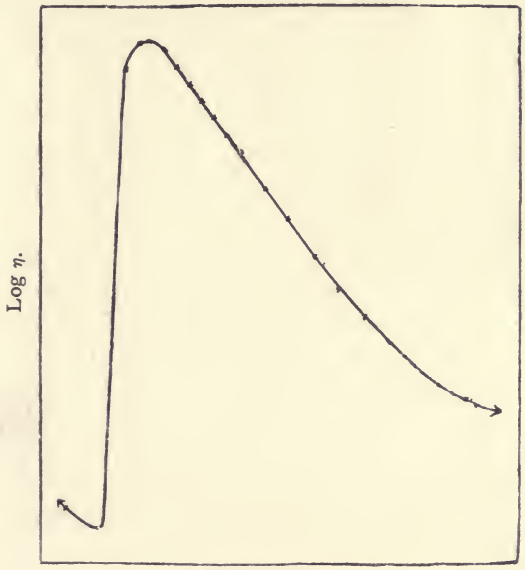


FIG. 12.

good in the majority of cases for low concentrations and for fairly coarse particles, discrepancies become apparent (1) at higher concentrations, and (2) with ultra-microscopic particles. Hatschek draws attention to the fact that the capillary viscometer, with its high rate of shear, may be responsible for the want of agreement, and further that nothing is known about the shape and density of ultra-microscopic particles, quantities which may conceivably be important in this connexion.

When, however, Couette's apparatus was used permitting a variable rate of shear the results obtained show a closer agree-

ment with theory. The same author considers that the volume of the adsorption envelope must be considered as well as that of the disperse phase itself, and calculates, using figures for sulphur sols, that the thickness of this layer is 0·87 $\mu\mu$.

In the case of emulsoids Hatschek[105], assuming that the velocity of displacement of juxtaposed layers exceeds a certain critical value, shows that the viscosity of an emulsoid η' is given by the equation $\eta' = \frac{\eta \sqrt[3]{A}}{\sqrt[3]{A'} - 1}$ where η is the viscosity of the dispersive medium and A is the ratio of the volume of the emulsoid to that of the disperse phase. When the values of A are compared with those of A′ which represent the ratio between the volume of the emulsoid to the weight of the disperse phase present, it is found that the ratio $\frac{A}{A'}$ is very nearly constant, leading to the conclusion that the disperse phase consists of the dissolved substance together with a definite and constant amount of the dispersive medium.

Other Applications.—The rate of coagulation of aluminium hydroxide sols by the addition of electrolyte has been followed by viscosity measurement. Freundlich and Ishizaka[104] find that the maximum viscosity of a sol, which is completely precipitated by an electrolyte increases with the quantity of the colloid in the sol. The maximum viscosity is further dependent on the nature of the precipitant, being smaller with NO_3 and CNS ions than with the sulphion and the succinate ion. Shaking and other mechanical disturbances change the viscosity of the concentrated sols.

The Nature of Aqueous Soap Solutions.—Soap solutions have a high electrical conductivity and fall into the class of electrolytic colloids, to which congo red, casein and many other compounds belong, and which are characterized by containing both colloidal and electrolytic constituents. McBain, Miss Cornish and Bowden[116] have shown that when electrolytes such as caustic soda are added to aqueous solutions of sodium palmitate the viscosity falls at first, reaches a minimum and then increases rapidly as the electrolyte concentration is still further increased. The initial diminution of viscosity may be due to the abstraction of water from the disperse phase, with a consequent diminution

in the bulk of the latter; the rapid increase in viscosity above a certain electrolyte concentration is due probably to the formation of colloidal aggregates, the size of which may increase with increasing concentration. Results similar to the above have been obtained by Goldschmidt and Weissmann [114] with solutions of soft soap, and these authors consider that the addition of electrolytes with a common ion in dilute solution diminishes the hydrolysis and degree of dissociation of the alkali salts of the fatty acids, whereas in higher electrolyte concentration the soap is largely present as a hydrophile colloid.

The Chemistry of Nitro-Cellulose.—Schwarz [103] determined the viscosity of solutions of nitro-cellulose in camphor-alcohol, ether-alcohol and in acetone. The viscosity increases very rapidly with concentration and the solutions exhibit the phenomena of ageing. The ageing is accompanied by a very considerable increase in the viscosity which is more pronounced in the case of the more concentrated solutions. Baker [102] in a similar investigation showed that the nitro-cellulose solutions follow the law $\eta = \eta_0 (1 + ac)$ when a and k are constants dependent on the nature of solvent and solute.

The Valuation of Rubber.—Schidrowitz [136] has shown that an intimate connexion exists between the mechanical properties of rubber and the viscosity of its solutions. Fol [101] pursuing the same line of work finds that violent shaking during the preparation of the solution affects the viscosity considerably. The results are affected by lapse of time, between making the solutions and carrying out the measurements, and by temperature.

CHAPTER VIII.

THE RELATION BETWEEN VISCOSITY AND CHEMICAL CONSTITUTION.

It has been pointed out in Chap. III. that the earlier workers experienced very considerable difficulty in establishing the additive nature of viscosity on account of the apparently erratic results afforded by certain of the substances examined. Particularly abnormal are the aliphatic alcohols and acids and, indeed, all hydroxylic compounds; but many other constitutive factors such as ring formation, branched chains, unsaturation (simple or conjugated), etc., exert a marked disturbing influence on the viscosity of a liquid.

So sensitive indeed is viscosity to constitutive changes that special care must be taken to eliminate as far as possible the influence of these when calculating atomic or group values, and the figures so obtained can only be used for calculating the viscosities of "normal" liquids.

The influence of the hydroxyl group in raising viscosity was first recognized by Gartenmeister and its action is no doubt intimately connected with the potential quadrivalence of the oxygen atoms inducing association. The effect it produces will be evident from the following figures.

TABLE XLVII.—Viscosity and Association.

Substance.	Viscosity (25° C.).
Ethane	gas
Ethyl alcohol	0·0109
Ethylene glycol	0·1733

Its influence again is very well illustrated by the steady increase in the viscosity of freshly distilled ethyl acetoacetate owing to the gradual enolization of the ketonic form.[96]

Since, however, the great exaltation of viscosity produced by the hydroxyl group is at any rate mainly due to association induced by the latent affinities of the oxygen atom we should

expect the introduction of another unsaturated group into the molecule to result in the partial neutralization of the residual affinity of the oxygen atom owing to mutual action of the two unsaturated centres. This would result in a reduction of the association and consequently to a diminution of the viscosity.

Moreover the diminution of association should depend on the degree of unsaturation of this second group and also on the degree of its proximity to the hydroxyl group.

The correctness of these views is clearly borne out by the numerical values obtained for a number of phenols and their derivatives.[96]

TABLE XLVIII.—Viscosity of the Phenols.

Substance.	Viscosity.	$\frac{\eta \times \text{Mol. Vol.}}{10^6}$
Phenol	0·0404	453
Anisole	0·00741	66·6
Phenetole	0·00825	63·8
p-Chlorophenol	0·0602	590
m-Chlorophenol	0·0472	459
o-Chlorophenol	0·0225	212
p-Cresol	0·0561	527
m-Cresol	0·0506	475
o-Cresol	0·0351	333
m-Tolyl methyl ether	0·00875	68·5
o-Tolyl methyl ether	0·00849	66·7
p-Tolyl methyl ether	0·00806	62·8
o-Nitrophenol	0·0234	199
Ethyl salicylate	0·0177	118
Benzyl alcohol	0·0301	286
Benzyl methyl ether	0·0103	81·1

It will be noticed that the value of the expression $\frac{\eta \times \text{Mol. Vol.}}{10^6}$ has been used in the above table as a means of comparison of the liquids employed and as an indication of the presence and the extent of association.

Dunstan[97] pointed out that in a number of series the members of which are similar in constitution and generally recognized as unassociated, the value of $\frac{\eta \times \text{Mol. Vol.}}{10^6}$ only varies between comparatively small limits. The average value for the lower alkyl chlorides is 37, for the bromides 51, for the iodides 68, for the ketones 43, and for the ethers 25. The values for

benzene, anisole, phenetole, and the three tolyl methyl ethers all lie between 60 and 70. On the other hand association enhances the value to a most marked extent, the numbers for water, ethyl alcohol and glycol being respectively 494, 193 and 2750, and the expression affords a fairly good test for molecular aggregation. Too much weight, however, must not be attached to the values afforded by this expression since it is undoubtedly only a first approximation, being influenced considerably by many other factors such as molecular symmetry, conjugation of unsaturated groups and linkings and ring formation.

Influence of Symmetry.—The figures in Table XLVIII illustrate a further constitutive influence on viscosity by the difference in the viscosities of the isomeric and presumably unassociated tolyl methyl ethers and benzyl methyl ether, the more compact molecules of the former exhibiting a distinctly lower viscosity. That this is an example of a very general rule is clearly shown by comparison of the viscosities of the following normal and *iso* compounds.

TABLE XLIX.—Effect of Symmetry on Viscosity.

Substance.	Viscosity (0° C.).	Substance.	Viscosity (0° C.).
n-Pentane . .	0·00283	*Iso*-pentane . . .	0·00273
Propyl iodide . .	0·00938	*Iso*-propyl iodide . .	0·00878
Methyl butyrate .	0·00759	Methyl *iso*-butyrate .	0·00672
Butyric acid . .	0·02284	*Iso*-butyric acid . .	0·01885
Butylamine . .	0·00681	*Iso*-butylamine . .	0·00553

Influence of Unsaturation.—Until the last twenty years the term unsaturation was almost exclusively employed to denote the presence of an ethylenic or acetylenic union. With the development of modern views on "residual affinity" and "latent valency," however, the scope of the term unsaturation has been very greatly widened. Accordingly, in view especially of the additional complications introduced by "conjugation" it will be advisable to consider separately the various effects produced by the manifestations of what is still a very vaguely understood phenomenon.

Dealing first with the influence of a simple ethylenic and acetylenic linkage one cannot draw any definite conclusions from the numerical data available. It may be stated that as a general

rule the presence of such groupings raises the viscosity above that of the corresponding saturated compound. The viscosity of the acetylenic compound, however, is sometimes greater and sometimes less than that of its ethylenic analogue. The following results are typical.[98]

TABLE L.—EFFECT OF UNSATURATION ON VISCOSITY.

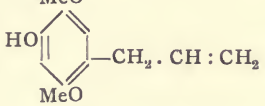
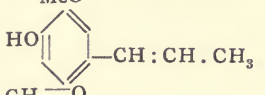
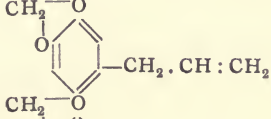
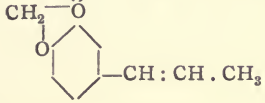
Substance.	Formula.	Viscosity (25° C.).
Propyl ethyl ether	$CH_3 . CH_2 . CH_2OEt$	0·00339
Allyl ethyl ether	$CH_2 = CH . CH_2 . OEt$	0·00345
Propargyl ethyl ether	$CH \equiv C . CH_2OEt$	0·00527
Phenyl ethane	$C_6H_5 . CH_2 . CH_3$	0·00607
Phenyl ethylene	$C_6H_5CH : CH_2$	0·01109
Phenyl acetylene	$C_6H_5C : CH$	0·00883

Very much more striking, however, are the effects produced by the alternation of double with single linkages (the "conjugated double bonds" of Thiele).

The abnormalities produced by the presence of such conjugated double bonds have been recognized in many physical properties but in none more markedly than in viscosity, which undergoes remarkable exaltation in conjugated compounds.

The following results[99] illustrate the effect on viscosity of conjugation of double linkage.

TABLE LI.—EFFECT OF UNSATURATION ON VISCOSITY.

Substance.	Formula.	Viscosity.
Acetone	$CH_3 . CO . CH_3$	0·00305
Mesityl oxide	$(CH_3)_2C = CH . CO . CH_3$	0·00876
Phorone	$(CH_3)_2C = CH . CO . CH = C(CH_3)_2$	0·0139
Eugenol		0·0693
Iso-eugenol		0·2672
Safrol		0·0229
Iso-safrol		0·0398

It is interesting to compare the effect of conjugation on other physical properties.

TABLE LII.—Effect of Conjugation of Double Bonds on Physical Properties.

Substance.	Molecular Refraction.		Optical Anomaly.	Mol. Volume.	Viscosity.	Boiling Point.
Acetone	observed	16·05	+ 0·01	73·8	0·00305	56
	calc.	16·04				
Mesityl oxide	observed	30·13	+ 0·74	114·6	0·00876	130
	calc.	29·39				
Phorone	observed	45·39	+ 2·66	153·9	0·0139	195
	calc.	42·73				
Eugenol	observed	48·1	+ 0·5	—	0·0693	247
	calc.	47·6				
Iso-eugenol	observed	49·3	+ 1·7	—	0·2672	260
	calc.	47·6				
Safrol	observed	45·9	+ 0·1	—	0·0229	232
	calc.	45·8				
Iso-safrol	observed	47·6	+ 1·8	—	0·0398	249
	calc.	45·8				

It might well be expected that conjugation of groups possessing notable residual affinity would produce a very similar effect in enhancing the viscosity of a substance. This is well illustrated by the following table which gives the viscosity (in amyl-acetate solution at equivalent concentration) of a number of derivatives of acetone.

TABLE LIII.—Effect of Conjugation of Unsaturated Groups on Viscosity.

Substance.	Formula.	Viscosity at $\frac{\text{Mol. Wt.}}{20}$ per cent Concentration.
Acetone	$CH_3 . CO . CH_3$	0·00752
Acetophenone	$CH_3CO . C_6H_5$	0·00808
Benzophenone	$C_6H_5COC_6H_5$	0·00892
Benzyl acetone	$C_6H_5CH_2 . CH_2 . COCH_3$	0·00830
Benzyl acetophenone	$C_6H_5CH_2 . CH_2 . COC_6H_5$	0·00877

By combining the effects due to the conjugation of unsaturated bonds and the conjugation of unsaturated groups we obtain very great exaltation of viscosity. The degree may be gauged if it is remembered that the solutions in Table LIV have half the concentration of those in Table LIII.

TABLE LIV.—Effect of Conjugation of Double Bonds and Unsaturated Groups on Viscosity.

Substance.	Formula.	Viscosity at $\frac{\text{Mol. Wt.}}{40}$ per cent.
Benzyl acetone	$C_6H_5 . CH_2 . CH_2 . CO . CH_3$	0·00811
Benzylidene acetone	$C_6H_5CH : CH . COCH_3$	0·00833
Benzyl acetophenone	$C_6H_5CH_2 . CH_2COC_6H_5$	0·00850
Benzylidene acetophenone	$C_6H_5CH : CH . CO . C_6H_5$	0·00866
Cinnamylidene acetophenone	$C_6H_5CH : CH . CH : CH . COC_6H_5$	0·00888
Dibenzylidene acetone	$C_6H_5CH : CH . CO . CH : CH . C_6H_5$	0·00893
Dicinnamylidene acetone	$C_6H_5CH : CH . CH : CH . CO . CH : CH . CH : CH . C_6H_5$	0·00934

The validity of the conclusions drawn from the above data regarding the influence of symmetry and of unsaturated linkages and groupings on viscosity have been tested by means of a large number of aliphatic and aromatic amines and their derivatives [100].

TABLE LV.—Viscosity of Aliphatic Amines.

Substance.	Viscosity.	$\frac{\eta \times 10^6}{\text{Mol. Vol.}}$
n-Propylamine	0·00353	42·9
Allylamine	0·00375	50·0
n-Butylamine	0·00681	70·8
Iso-butylamine	0·00553	56·8
Diethylamine	0·00367	36·2
Di *iso*-butylamine	0·00687	40·0
Triethylamine	0·00363	26·1

TABLE LVI.—Viscosity of Aromatic Amines.

Substance.	Viscosity (55°).	Viscosity (130°).	$\frac{\eta_{55} \times 10^6}{\text{Mol. Vol.}}$	$\frac{\eta_{130} \times 10^6}{\text{Mol. Vol.}}$
Aniline	0·0171	0·00555	182	56·5
Methyl aniline	0·0108	—	96·9	—
Dimethyl aniline	0·00844	—	64·7	—
Allyl aniline	0·0141	0·00506	101	34·2
Benzyl aniline	0·0539	0·0120	306	64·5
Diphenylamine	0·0466	0·0104	266	61·1
Triphenylamine	—	0·0640	—	262
Benzylidene aniline	0·0399	—	229	—
Acetanilide	—	0·0190	—	142
Methyl acetanilide (at 120° C.)	—	0·00818	—	53·6
Benzylamine	—	0·00442	—	37·0
Dibenzylamine	—	0·00812	—	39·5
Tribenzylamine	—	0·0209	—	69·9
Methyl diphenylamine	—	0·00812	—	34·2

From the above figures which are drawn from a much larger number quoted in the original papers ample confirmation is obtained of the recognized influence of symmetry and conjugation of unsaturated nuclei.

The effect of replacing the hydrogen atoms of the amino group by alkyl radicles is steadily to diminish the viscosity whether the primary amine be aliphatic or aromatic. The effect of symmetry of the alkyl group in the isomeric normal, and isobutylamines has already been pointed out.

The results obtained for the aromatic amines, however, are particularly interesting in illustrating the effect of accumulating unsaturated nuclei. Whereas methylaniline and dimethylaniline are much less viscous than aniline, substances such as phenylaniline, benzylaniline, benzylidene aniline, acetanilide and especially triphenylamine have notably high viscosities. Exactly parallel are benzylamine, dibenzylamine and tribenzylamine. It is evident that here the exaltation due to accumulation of unsaturated nuclei more than counteracts the depression which might be expected owing to increased symmetry. That this latter influence is, however, still perceptible even in the highly conjugated compounds is evident when one compares diphenylamine and acetanilide with methyldiphenylamine and methylacetanilide.

The effect of introducing various substituent groups into the phenyl group of aniline and its derivatives has been studied by Thole (loc. cit.), the results in general following those previously described in connexion with the substituted phenols.

CHAPTER IX.

SOME APPLICATIONS OF VISCOSITY.

THE value of a physical property in the eyes of the average chemist depends largely on its applicability to problems which arise in the various branches of chemistry and which sometimes cannot be definitely solved by purely chemical methods.

Mention need only be made of the application of refractivity and absorption spectra to the classical controversies concerning the constitutions of ethyl acetoacetate and of isatin and of the work of Patterson, Lowry and others on the connexion between rotatory power and velocity of chemical reaction. Since viscosity is so highly a constitutive property it may and has been applied to a number of problems arising in physical, inorganic and organic chemistry and has proved particularly useful in certain cases such as in determining the constitution of the acetaldehyde phenylhydrazones where chemical evidence is not available.

Measurement of Rate of Reaction.—Since the viscosities of different substances are as a rule widely different, it is evidently possible to follow the course of a reaction by determining the viscosity of the reacting materials at definite intervals of time. It is necessary, of course, that the reaction should proceed to a small extent only during each viscosity observation though in some cases it is possible to examine more rapid reactions by removing samples of the reacting mixture at definite times, stopping the reaction by diluting, for example, with a cold solvent and then measuring the viscosity of the resulting solution.

The first worker in this direction appears to be von Schroeder,[117] who in 1903 found that the viscosity of a hot aqueous solution of gelatine slowly fell owing to hydrolysis of the gelatine. He found that $\frac{d\eta}{dt} = K(\eta_1 - \eta_2)$ indicating a monomolecular reaction.

Dunstan and Mussell [118] in 1911 applied the method to the following reactions: Freshly distilled acetoacetic ester (ketonic) → equilibrium mixture; aniline + ammonium thiocyanate → phenyl thiocarbamide; ammonium cyanate → carbamide; ammonium thiocyanate → thiocarbamide; acetic anhydride + water → acetic acid; benzoyl chloride + water → benzoic acid.

Two typical sets of figures will give an indication of the results obtained.

TABLE LVII.—Change of Ammonium Cyanate into Carbamide (in Aqueous Solution at 25° C.).

Time in Minutes from Middle of First Observation.	Time of Flow.	$a - x$.	$\frac{1}{t}\log_{10}\frac{a}{a-x}$.
0	4·29″	36·0	—
50	4·30″	35·0	0·00024
120	4·32″	33·0	0·00031
238	4·34″	30·4	0·00031
247	4·35″	30·0	0·00032
290	4·36″	29·0	0·00032
350	4·38″	26·7	0·00037
560	4·45″	20·0	0·00045
after 3 days	5·5″	—	—

It may be concluded, therefore, that this reaction is not unimolecular, a result in agreement with those of Walker, Hambly, Kay and Wood.

TABLE LVIII.—Hydrolysis of Benzoyl Chloride by Water (in Acetone Solution).

Time in Minutes.	$\frac{1}{t}\log_{10}\frac{a}{a-x}$.
11·5	—
14·5	0·0095
22·5	0·0102
44·5	0·0095
53·0	0·0096
80·0	0·0103
140·0	—

The values in the last column agree sufficiently well to indicate a reaction of the first order.

Determination of Transition Points.—If saturated solutions of a substance at a series of temperatures are prepared and the viscosities of these solutions plotted against the temperatures, a

smooth curve is in general obtained. If, however, the chemical composition of the substance changes at some point within the temperature range chosen the viscosity of the solution will naturally change and the temperature of transition will be indicated by a singular point on the viscosity-temperature curve. Hence viscosity measurements can be added to the already well-known dilatometric and solubility methods for determining transition points, and the results obtained by the various methods agree well.

The curves obtained on examining the classical cases of sodium sulphate and sodium carbonate [119] indicate clearly the transition of $Na_2SO_4 . 10\ H_2O$ to Na_2SO_4 and of $Na_2CO_3 . 10\ H_2O$ to $Na_2CO_3 . 7\ H_2O$ and $Na_2CO_3 . H_2O$.

Detection of Association and Conjugation.—The effect of these molecular influences on viscosity have been dealt with previously (pp. 72-75), and it need merely be repeated that both produce a very marked exaltation in the viscosity coefficient.

The Existence of Racemic Compounds in the Liquid State.—This problem has been the source of much controversy, and many methods have been suggested to decide whether a racemate on fusion or solution is converted into a mixture of the antipodes or whether it retains its individuality.

The bulk of the evidence is very unsatisfactory, usually because dilute solutions of the racemate have been investigated and this condition would tend to promote dissociation of the racemate.

Thus comparisons of affinity constants, molecular weights by the cryoscopic method and absorption spectra of *d*-, *l*- and racemic tartaric acids in dilute solution show no indication of the presence of the latter substance. On the other hand measurements of colour intensity, molecular weight, density, and absorption spectrum in concentrated solutions show in many cases undoubted signs of the existence of a racemic compound in solution.

Viscosity was first applied to the question by Beck [120] who examined fused mixtures of dextro and lævo camphoroxime. He found that the viscosities of the antipodes of the inactive mixture were identical. The same results were obtained with the oximes of the carvones showing that in neither of these cases is any racemic compound produced. These results might be expected from the shape of the fusion point curves determined

by Adriani for similar mixtures, and have been confirmed by subsequent viscosity measurements of the fused and also of the dissolved components.[121] The same investigator also carried out series of measurements with fused dimethyl-*d*-tartrate and racemate and with the acetyl derivatives of these esters.

TABLE LIX.—Viscosity of Dimethyl-d-Tartrates—Dimethyl Racemate Mixtures.

Per cent of Dextro-ester.	$\eta_{85°C.}\left(\eta^{25°C.}_{H_2O}=1\right)$.
100	14·023
95	14·251
80	13·971
50	14·580
0	14·464

TABLE LX.—Viscosity of Acetyl Dimethyl-d-Tartrate—Acetyl Dimethyl Racemate.

Percentage of Dextro-ester.	$\eta_{104°C.}\left(\eta^{25°C.}_{H_2O}=1\right)$.
0	6·764
10	6·666
40	6·912
100	6·933

Beck considered that in both series the viscosity values remain sufficiently constant to show complete dissociation of the racemic ester. Thole,[121] however, has pointed out that Bruni's cryoscopic measurements in ethylene dibromide solution undoubtedly demonstrate the possibility of actual existence of the dissolved racemic esters and that in Table LX the viscosity values with one exception seem rather to point to the inactive ester having a distinctly different viscosity from the active compound.

He examined several pairs of esters and considers that distinct indications are afforded of the existence of liquid racemates. Evidence of this is afforded by the following table.

TABLE LXI.—Viscosity of Racemates.

Ester.	Temperature.	Viscosity.
Methyl *d*-tartrate . . .	85°	0·133
Methyl racemate . . .	85°	0·130
Ethyl *d*-tartrate . . .	25°	1·457
Ethyl racemate . . .	25°	1·360
l-Methyl *l*-mandelate . .	85°	0·0632
l-Methyl *dl*-mandelate . .	85°	0·0653

The free tartaric and mandelic acids were also investigated, in the latter case a number of different solvents being used in order to find what dissociating influence these had.

The viscosity-concentration curves for aqueous solutions of active and racemic tartaric acids show that the amount of undissociated racemic acid increases with increasing concentration.[122]

Stewart had previously found that the absorption spectra curves of similar solutions of dextro and racemic tartaric acid are at low concentrations identical but at higher concentrations (about 14 per cent) show a distinct divergence.

In dissociating solvents such as water and pyridine no difference is to be found between active and inactive mandelic acids, but in a comparatively non-dissociating solvent such as amyl acetate curves similar to those of the tartaric acids are obtained.

The viscosimetric examination of a number of active and inactive alcohols and other substances has shown, however, that the free existence of a liquid or dissolved racemic compound is very exceptional.

The Viscosity of Geometrical Isomerides.—The first attempt to correlate geometrical isomerism with viscosity was made by Lauenstein [123] who, working with the sodium salts of certain dibasic ethylenic acids, could find no regularities, sodium maleate being less viscous than sodium fumarate, whilst with the methyl derivatives of these acids the reverse holds. These results are, however, complicated by the different degrees of ionization of the salts.

A much more complete investigation has been carried out by Thole [124] who examined the ethylenic acids and the esters, and also a number of oximes and phenylhydrazones, both in the dissolved and in the fused conditions.

The results obtained indicate that the viscosity and other

physical properties depend on the relative positions in the molecule of the two groups which exhibit most residual affinity, and a most convenient uniformity is gained by describing those compounds in which these groups approach each other as "adjacent" compounds and their isomerides as "opposed". Thus benz*anti* aldoxime is a typical "adjacent" compound and fumaric acid an "opposed" compound.

TABLE LXII.—Viscosities of Geometrical Isomerides.

Substance.	Configuration.	Solvent.	Viscosity.
Maleic acid	adjacent	methyl alcohol	0·005805
Fumaric acid	opposed	,, ,,	0·005887
Citraconic acid	adjacent	,, ,,	0·005908
Mesaconic acid	opposed	,, ,,	0·005905
Oleic acid	adjacent	amyl acetate	0·009549
Elaidic acid	opposed	,, ,,	0·009740
α-Bromo cinnamic acid	,,	,, ,,	0·008717
α-Bromo-*allo*-cinnamic acid	adjacent	,, ,,	0·008674
Ethyl maleate	,,	—	0·03016
,, fumarate	opposed	—	0·02455
,, citraconate	adjacent	—	0·03251
,, mesaconate	opposed	—	0·02399
,, oleate	adjacent	—	0·08948
,, elaidate	opposed	—	0·08175
,, oleate	adjacent	amyl acetate	0·009260
,, elaidate	opposed	,, ,,	0·009144
Benzaldehyde-α-phenyl hydrazone	,,	,, ,,	0·008785
Benzaldehyde-β-phenyl hydrazone	adjacent	,, ,,	0·008930
Acetaldehyde-α-phenyl hydrazone	—	—	0·008353
Acetaldehyde-β-phenyl hydrazone	—	—	0·008378
Camphor quinone-α-phenyl hydrazone	opposed?	chloroform	0·006635
Camphor quinone-β-phenyl hydrazone	adjacent?	,,	0·006334
α-Benzaldoxime	,,	amyl acetate	0·008374
β-Benzaldoxime	opposed	,, ,,	0·008433
α-Anisaldoxime	adjacent	,, ,,	0·008640
β-Anisaldoxime	opposed	,, ,,	0·008725
α-Piperonaloxime	adjacent	,, ,,	0·008849
β-Piperonaloxime	opposed	,, ,,	0·009160
α-Benziloxime	adjacent	,, ,,	0·009300
β-Benziloxime	opposed	,, ,,	0·009402

Where a solvent was used the viscosities quoted are those of solutions of concentration $\frac{\text{mol. wt.}}{40}$ per cent of solute.

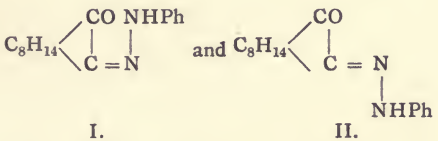
Summing up these results this worker concludes that the viscosities of the isomers depend not only on the relative positions of the unsaturated groups but also on the degree of residual affinity they possess. Where these radicles possess small residual affinity the opposed compound has a lower viscosity than the adjacent

isomeride. This result is indeed to be expected since in the latter a tendency to potential ring formation will exist, a condition which is well known to enhance viscosity values.

On the other hand, when the groups possess a considerable degree of residual affinity as in the dibasic ethylenic acids, the exaltation of viscosity due to potential ring formation is masked by the depression of viscosity due to intramolecular neutralization of the residual affinities and consequent inhibition of molecular association, the result being that the adjacent compound has the lower viscosity. It is interesting to note in this connexion that barium fumarate crystallizes with three molecules of water while barium maleate, in which the residual affinities of the carboxyl groups are more nearly mutually satisfied, combines with only one molecule of water.

The value of these conclusions shows itself when they are applied to the hitherto unproved and in one case unknown constitutions of certain geometrically isomeric phenylhydrazones.

Thus in the case of the two camphorquinone phenylhydrazones

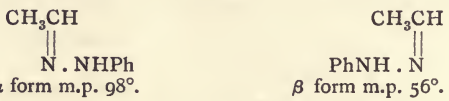


I. II.

it is highly probable that the form I in which the carbonyl and NHPh groups are adjacent will have the lower viscosity. Measurement showed that the lower melting, more soluble isomer had the lower viscosity and this form therefore will have the adjacent constitution I. By analogy with other camphor derivatives, though without any direct evidence, this same configuration was assigned by Forster and Zimmerli [125]. The configurations of the benzaldehyde phenylhydrazones have been proved by chemical means and the adjacent form possesses the higher viscosity, showing that the effect due to potential ring formation is greater than that due to inhibition of association. This is due to the small residual affinity of the phenyl group as compared with that of the carbonyl group in the case just considered.

With the data now available one can approach the difficult problem of the configuration of the two acetaldehyde phenylhydrazones. If ordinary acetaldehyde phenylhydrazone is crystal-

lized from alcohol containing a trace of acid it separates as the so-called β form melting at 56°. In the presence of a trace of alkali, however, the α form melting at 98° is obtained.* These changes take place so readily that the determination of the configuration by chemical methods is almost impossible, but measurement of the viscosities of solutions of the isomerides shows that the α form has the lower viscosity. Now since the methyl group undoubtedly possesses less residual affinity than the phenyl residue in the benzaldehyde phenylhydrazones the isomeride of lower viscosity should be the opposed compound. The following configurations may therefore be assigned to these compounds.



* It has been suggested that the differences are due to dimorphism and not to geometrical isomerism. The different viscosities of the solutions effectually dispose of this argument.

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